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PICATINNY ARSENAL

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1.1 PREPARATION; PROPERTIES; REACTIONS

Hydrazine Perchlorates

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The four hydrazine perchlorates, viz. hydrazine perchlorate and its hemihydrate, and hydrazine diperchlorate and its dihydrate have been made in quantities of a few hundred grams from hydrazine and "Analar" grade sixty per cent perchloric acid. The monoperchlorate presents little difficulty; the extreme impact sensitiveness which has been reported (with F.I. worse than lead azide) has not been found even on material shown by the Karl Fischer test to be anhydrous.

The dihydrate of hydrazine diperchlorate is also easy to obtain by mixing the cooled constituents. It is best dehydrated by low pressures (0.01 tor) at room temperature with a liquid nitrogen trap or phosphorus pentoxide to take up the water; it is not easy to avoid loss of some perchloric acid, and the analysis is often low in acid (the second perchloric acid titrates in aqueous solution as free acid). No solvent has been found for recrystallization of the anhydrous material; it hardly dissolves in liquid sulphur dioxide, and loses perchloric acid on washing with ether, tetrahydrofuran, and many others.

The mono and diperchlorates may be distinguished by analysis. Some separation occurs on flotation, since the diperchlorates have densities above 2.0, and will sink in dibromopropane, in which the monoperchlorates float. The optical properties have been determined, but are not very helpful for diagnosis, as all three indices for each of the four compounds fall within the range 1.51 to 1.53. The diperchlorate dihydrate is biaxial negative with $2E = 68^\circ$ for red, 71° for yellow, 80° for green and 88° for blue. Extinction in acicular crystals was parallel, with the slower vibration along the length, and the intermediate vibration across it.

Double Perchlorates

Addition of hydrazine to an aqueous perchloric acid solution of lead perchlorate gave a crystalline precipitate containing lead, hydrazine and perchlorate; it is extremely easy to ignite, and to initiate by blows. It may be a basic compound. Its sensitivity to impact and to friction resemble those of normal lead styphnate.

Nitric Ester Research

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Glycerol 1-nitrate, prepared by hydrolysing glycidol nitrate and by partial nitration of glycerol, has been characterised as the benzoate, m.p. 68°C , 4-nitrobenzoate, m.p. 137°C , 3,5-dinitrobenzoate, m.p. 127°C , and 4-methoxybenzoate, m.p. 105°C . The isomeric glycerol 2-nitrate, m.p. 54°C , was obtained by treating the mixed mononitrates with periodic acid to remove glycerol 1-nitrate; glycerol 2-nitrate di-4-nitrobenzoate, m.p. 152°C , has been prepared.

Nitration of glycidol nitrate in dioxane gave impure glycerol 1,3-dinitrate, identified as the 4-nitrobenzoate, m.p. 95°C .

/R_F

R_F values have been determined for a number of nitric esters by paper partition chromatography using n-hexane or n-octane/methanol or ethanol/water as mobile phase. The yellow colour produced by ultraviolet irradiation of the paper after spraying with ethanolic diphenylamine was used to locate the nitric esters. The method is a very sensitive test for the presence of lower nitric esters in NG, DEGN, TEGN, etc. For example, glycerol dinitrate can be detected in NG at a concentration of 1 in 25,000 (wt/wt).

Chromatographic examination of glycerol 1,2-dinitrate, prepared from glycerol 1,2-dibromohydrin (E.R.D.E. TR.1/61, p.33) and from allyl alcohol (with iodine/silver nitrate) showed the presence of two non-hydroxylic impurities which were separated by preparative chromatography on cellulose powder and identified as NG and a carbonyl-containing nitric ester, possibly glyceraldehyde dinitrate.

Careful measurement of the ultraviolet absorption spectra of the glycerol nitrates in water over the range 210 - 230 μ has shown that molecular extinction coefficients increase in the order 1- ~ 2- < 1,2- < 1,3- < 1,2,3-. However, an earlier claim that an additive relationship exists between the extinction coefficients has not been substantiated. The effect of hydrogen bonding in aqueous solution is being investigated by repeating the measurements using a non-polar solvent.

Nitramine Chemistry

CONFIDENTIAL

Ammonium and hydrazinium salts of primary nitramines are being prepared for assessment as ingredients of double-base propellants. Salts of ethylenedinitramine (Table 1) were obtained by adding base to a solution of the nitramine in dimethylformamide; the dihydrazine salt of methylenedinitramine was prepared in isopropanol.

TABLE 1

Properties of Some Nitramine Salts

Nitramine	Salt	Melting Point, C	Relative Median Height h(50%), 2 kg., (RDX = 80), cm.	H_f (constant pressure), kcal/mole
EDNA	$O_2N=N(CH_2)_2N=NO_2(NH_4)_2$	177° - 178° (decomp.) needles from $H_2O/MeOH$	> 350	-81.2
EDNA	$O_2N=N(CH_2)_2N=NO_2(N_2H_5)_2$	138° - 139°, needles from $H_2O/MeOH$	> 350	-29.6
MEDNA	$O_2N=NCH_2N=NO_2(N_2H_5)_2$	107°, plates from $H_2O/isoPrOH$	100	-43.7

/Ultraviolet

Ultraviolet Irradiation of RDX

RESTRICTED

Preliminary experiments have been carried out using fused quartz and pyrex glass irradiation vessels. 10 g. of acetone-recrystallised RDX was used in each experiment and provided a complete layer over a surface of approximately 35 cm². A 250-watt Hanovia lamp without filter, nine inches above the surface of the RDX, was used as light source and the irradiation vessels were cooled from below by a stream of cold water. A slow stream of either air or nitrogen was used to sweep the gaseous products of the reaction into vigorously stirred water maintained at pH 7.5 to 9.0 by periodic addition of 0.1 N NaOH solution.

In the earlier experiments, indicators were used to control pH, but all those tried were found to become insensitive or were subject to abnormal colour change. The results obtained were quantitatively unreliable, but indicated that the rate of reaction, as measured by the evolution of acidic gas was at least 50 per cent faster in the quartz vessel. The characteristic pale yellow colour acquired by RDX on irradiation with u.v. radiation was visible in the quartz vessel after three hours exposure, whereas the same stage was reached in the glass vessel in seven hours.

Further work has been carried out in the quartz vessel only, a glass electrode and pH meter being used as control. Two prolonged irradiations with disturbance of the surface layer of RDX every 48 hours, have been carried out, one with nitrogen as the sweeping gas, the mean titre being 0.33 ml. 0.1 N NaOH per hour. When air was used, the mean titre was 0.43 ml. of 0.1 N NaOH per hour. The products have been examined qualitatively and in each case contain nitrite and nitrate.

Apparatus

The introduction of a thin-walled stainless steel tube of elliptical cross-section into the tube of the 10-g. scale four-stage zone melter has prevented tube fracture in all experiments, even with materials which normally result in fracture after a few passes.

The design and production of laboratory equipment includes:

- (a) Set-point apparatus with thermistor for temperature measurement,
- (b) Miniature hot plate with thermometer and sensitive control,
- (c) Design and preliminary production work on a Dennis-type melting point bar for temperatures up to 500°C,
- (d) Collaboration in design of 1-kg. scale zone melting apparatus,
- (e) Rotary solid feed for small-scale continuous laboratory preparations.

Miscellaneous Preparations

CONFIDENTIAL

2-Nitroethanol was obtained by the base-catalysed condensation of nitromethane with formaldehyde at 70°C. Hazard appraisal tests showed that the compound is insensitive to impact [relative median height h 50 per cent (2 kg.) 98.4 cm.; nitromethane, 90 cm.; ethyl nitrate, 43 cm.] and is

/relatively

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relatively stable to heat (decomposes between 204° and 240°C). However, distillation of 2-nitroethanol is particularly hazardous at the beginning and end of the process.

Di(β -cyanoethyl)2,3-dihydroxypropylamine, the C-1 diol used to improve low temperature properties of polyurethane propellants, has been prepared by reaction between acrylonitrile and 2,3-dihydroxypropylamine; β -cyanoethyl-2,3-dihydroxypropylamine was identified as an intermediate product of the cyanoethylation. Measurement of infrared spectra and calculation of the ratio of peak optical density of the methyl band to peak optical density of the nitrile band is a convenient method of following the reaction. The structure of the products was confirmed by preparing 4-nitrobenzoyl derivatives and examining their infrared spectra. Acetone reacts with di(β -cyanoethyl)2,3-hydroxypropylamine to form an isopropylidene derivative.

3-Nitrazapentane-1,5-di-isocyanate, a low temperature curing agent for polypropylene glycols, has been prepared by the route:

acrylonitrile/ammonia \longrightarrow di(β -cyanoethyl)amine \longrightarrow
di(β -cyanoethyl)ammonium nitrate \longrightarrow di(β -cyanoethyl)nitramine \longrightarrow
di(β -carboxyethyl)nitramine \longrightarrow acid chloride of di(β -carboxyethyl)nitramine
 \longrightarrow acid azide of di(β -carboxyethyl)nitramine \longrightarrow 3-nitrazapentane-
1,5-di-isocyanate (see also p.21).

The preparation of trinitrophloroglucinol (TNPG) by a continuous process was developed. Some 13 kg. of TNPG were made, with an ultimate production rate of 250 g. per hour. 150 g. of 2,2-dinitropropan-1,3-diol were prepared. The reaction of ethylenediamine with bifunctional nitroaromatics, such as 1,3-dimethoxytrinitrobenzene, gives explosive products with melting points above 360°C.

1.2 PILOT-SCALE OPERATION AND PRODUCTION. INVESTIGATION OF PROCESSING AND HANDLING METHODS

Polyesters

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Four new polyesters have been made in the 5-gallon reactor for trials in propellant. A difficulty has been encountered in making polyester from tripropylene glycol: the reaction is very slow and low acid numbers seem to be unattainable. Attempts to reduce acid number by increase in temperature led to lowering of the hydroxyl number without any corresponding decrease in acid number. It is thought that this may be due to polymerisation of the glycol itself with elimination of water.

The rapid method of determining hydroxyl numbers has been covered by patent and N.R.D.C. is considering its exploitation.

Lead Salts

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260 lb. of lead phthalate and 600 lb. of "lead stannate" have been made during the period. Initial ballistic results on 30-lb. batches of "lead stannate" using centrifugal pump mixing with recycling show encouraging reproducibility and at pH 6.0 to 6.2 give the desired burning rate

/characteristics

characteristics. The inverse relationship between bulk density and strand burning rate for pump mixing continues to be valid; a bulk density of 1.7 g/cm³ gives the desired properties.

The effect of dilution on the process has been further explored under conditions of good mixing, and bulk densities as low as 0.8 g/cm³ have been obtained using high liquor recycle rates and low feed rates. This corresponds to a strand burning rate of 1.1 to 1.2 inches/sec., which may prove to be the maximum obtainable on present knowledge.

It is felt that the reproducibility at low concentrations may not be so dependent on efficiency of mixing as it is at higher concentrations. This is being investigated in the laboratory.

Recovery of Acetic Acid from HMX Waste Acid

RESTRICTED

Investigations continued with an examination of R.O.F. plant acid. It analysed to acetic acid 56.9 per cent, formaldehyde 1.35 per cent, formic acid 0.65 per cent, ammonium nitrate etc. 3.3 per cent, nitric acid 1.74 per cent. Controlled thermal decomposition with sulphuric acid showed that most of the available nitrogen is evolved as nitrogen and nitrous oxide, only 5 per cent as nitric oxide in strong acid but increasing to 35 per cent in weak sulphuric acid. Similar experiments using synthetic mixtures showed that nitric/acetic/sulphuric acid produced no nitric oxide while nitrous/acetic/sulphuric acid mixtures produced at most 50 per cent of the nitrogen as nitric oxide. Introduction of air to the plant would reoxidize this to NO₂ which could degrade more acetic acid; but in the absence of air the acetic acid loss has been measured as about 3 per cent and with air introduced it could only increase to about 5 per cent.

Thus laboratory work has shown that the chemical loss of acetic acid by this recovery process should not exceed about 5 per cent, and has shown a possible mechanism for it. It is understood that R.O.F., Bridgwater have now reduced their total loss to about 7 per cent. The reactions with formaldehyde and formic acid have been studied in an endeavour to elucidate the mechanism of the fume-off reaction, but a complete picture has not been obtained as the system is too complicated.

Evaporative Solvent Nitration

CONFIDENTIAL

Further development of the novel process described in E.R.D.E. TR.2/62 required information on the mutual solubility of the fluorocarbon solvents and sulphuric/nitric mixed acids over a range of water contents. Part of this information has now been obtained for trichlorofluoromethane and dichlorofluoromethane in an apparatus devised to enable the determination to be made at the boiling point of the solvent. It has been shown that these two solvents possess a high resistance to hydrolysis and, using mixed acids up to 80 per cent concentration and refluxing for 7 hours, only one experiment has indicated slight attack on the solvent, shown by the presence of chloride in the mixed acid. Further examination pointed to an impurity in the particular supply of solvent. The information will be used to calculate the optimum nitration conditions for ethylene, diethylene and triethylene glycols.

/Ammonium

Ammonium Perchlorate

RESTRICTED

The ammonia/carbon dioxide process and the recrystallisation plant have been the subject of discussion with R.O.F. Bishopton, but the proposals made have not yet been implemented.

Recrystallisation of a considerable quantity of ammonium perchlorate continued, bringing the total treated to over four tons. In all work where the evaporative recrystalliser was used, with one exception, there has been a consistent improvement in the curing rate of a polyurethane propellant using the purified material. The exception was a recent batch of American material and this is being examined carefully for impurities. It now seems likely that impurities in only trace quantities are involved, and that these affect polyester but not polyether systems.

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2.1 EVALUATION

2.1.1 Analytical

Determination of Cryolite in Cordites

UNCLASSIFIED

The cryolite content of a cordite is normally estimated by the determination of the sodium or potassium content. A micro-analytical technique has been developed utilising the oxygen flask method of combustion, followed by a fluoride ion determination on the absorbing liquid. It is essential that aluminium ions be removed from the solution by ion exchange because they interfere with the thorium nitrate titration which is used as the final stage of the estimation. Both N and SUK cordites containing from 0.3 to 2 per cent cryolite have been analysed successfully by this method.

A colorimetric method for the determination of the fluoride ion content would be preferable, hence further work is being carried out with this object in view.

2.1.2 Compatibility, Stability and Climatic Testing

Stabilisation by Resorcinol

CONFIDENTIAL

The mechanism of the conversion of nitroso-aromatics to nitroaromatics in stabilisation processes is being studied by the use of ^{15}N enriched materials. In preliminary experiments with unlabelled materials, it has been found that nitric acid, prepared in situ from potassium nitrate and sulphuric acid, will not convert 2,4-dinitrosoresorcinol to the corresponding dinitro compound. However, if a catalytic amount of nitrite ion is added the conversion takes place.

Reaction of Stabilisers with Alkoxyl Radicals

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It has been shown that the first step in the thermal decomposition of nitric esters is fission of the O-NO₂ bond:



Hitherto, attention has been focussed on the reactions of the oxides of nitrogen formed thereby, but very little study has been made of the alkoxyl radicals. An approach to this aspect of the problem is being made by examining the reaction between t-butoxy radicals, generated from t-butyl peroxide, and diphenylamine. A complex mixture is formed, from which has been isolated a material of the formula C₂₄H₁₄ON. Similar reactions appear to take place with other stabilisers such as carbamite.

Stability of Ball Powders

UNCLASSIFIED

Recent ball powder compositions, although containing nitroglycerine, use diphenylamine as stabiliser. This is contrary to normal British

/practice

practice, diphenylamine having been considered for many years to be incompatible with nitroglycerine. In order to obtain more specific information, heating trials were commenced to compare the rates of disappearance of diphenylamine and other stabilisers, in simple two-component mixtures with nitroglycerine. Preliminary results for 70° and 80°C, with mixtures containing one per cent of stabiliser, showed that the molar rate of disappearance of diphenylamine was four to six times greater than that of 2-nitrodiphenylamine. In the latter case the results agreed well with the rate of evolution of dinitrogen tetroxide from nitroglycerine measured by the Will test at these temperatures. It would appear from these observations that, while there is a direct bimolecular reaction between nitroglycerine and diphenylamine, with 2-nitrodiphenylamine the rate-determining step is the thermal decomposition of the nitroglycerine. Since the ball powders in question contained only 10 per cent nitroglycerine, their stability is expected to be satisfactory.

Chemical Stability of Igniter Composition for Carl Gustav 84-mm Anti-Tank Weapon CONFIDENTIAL

A mixture of one part of gunpowder with three parts of a Bofors ballistite flake, containing NG and NC, and stabilised with diphenylamine (1 per cent) plus carbamite (0.5 per cent) is used as the igniter in this weapon. Experiments to measure the rate of fall of stabiliser at 120°F (49°C) showed that the diphenylamine content fell about ten times as fast as that reported for American ballistites stabilised with diphenylamine, and also at ten times the rate expected from the trials on mixtures of diphenylamine and nitroglycerine at 120°F reported above. No satisfactory reason for this behaviour has yet been found.

In contrast, the rate of disappearance of carbamite at 80°C was apparently normal. Very little carbamite was used up until the diphenylamine had been converted to its di- and trinitro-derivatives, and the fall in carbamite content then proceeded at a similar rate to British ballistite B at the same temperature. In view of the behaviour of the carbamite, the stability of this composition must be considered satisfactory, but the omission of diphenylamine would appear desirable, perhaps with compensating increase in the proportion of carbamite.

Thermal Decomposition of Nitroglycerine UNCLASSIFIED

It has been reported (E.R.D.E. Report No. 21/R/62) that the evolution of dinitrogen tetroxide, from nitroglycerine heated at temperatures between 75° and 85°C in the Will test apparatus, proceeds initially at a slow rate, and then accelerates to a constant rate after a few hours. Attempts to confirm this observation have been unsuccessful, except for the particular sample used in the original work. With other samples the initial "inhibition" period is much less pronounced, in some cases not observed, and the constant rate stage of N₂O₄ evolution is reached much more quickly. When reached, the constant rate has, for most samples, the same value as was found for the first specimen.

The inhibition period was presumed to have been caused by the presence in the NG of an impurity which either inhibited the breakdown of the ester, or was capable of reacting with dinitrogen tetroxide as it was produced. Attempts to correlate these results with the probability of such an impurity

/by

by studying NG samples of different histories, have so far not proved successful.

2.1.4 Mechanical and Rheological

Studies on Polyurethane Propellant Mix Viscosities

CONFIDENTIAL

Earlier studies, using an influx viscometer, have shown that aluminium/polyester slurries show Newtonian behaviour at concentrations up to 55 per cent by volume; the viscosity at this concentration is about 9000 poises at 25°C - some 1400 times greater than the viscosity of the polyester. At still higher concentrations, the slurry becomes non-Newtonian and the apparent viscosity rises rapidly to more than 100,000 poises, as close packing is approached. In this region, errors and secondary effects in the viscometer become larger, and confirmatory measurements are desirable. Tests have therefore been carried out on a conical-cylindrical viscometer; agreement in the Newtonian region is good. In the non-Newtonian region the differences are greater, and are probably due to the difficulties of making and keeping slurries of a uniform, precisely known, high concentration.

The Fatigue Behaviour of Polyurethane Propellants

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The cantilever bend fatigue apparatus has been used to study the behaviour of three sets of polyurethane propellants; each set consisted of three or four propellants of the same basic composition but with different equivalence ratios of tolylene di-isocyanate (TDI) to polyester.

The relation between fatigue life and temperature passes through a sharp maximum at about -20°C; this temperature is independent of equivalence ratio, or polyester type. Fatigue life at this temperature increases five-fold as the equivalence ratio is lowered from 0.90 to 0.83 for an L.77 type (based on iso-sebacate) and by a similar amount as the ratio is lowered from 0.80 to 0.75 for an L.81 type (based on azelate).

The curves of peak fatigue life versus equivalence ratio are parallel, but not coincident. This is because different batches of polyester give different binder moduli for a given equivalence ratio. Fatigue lives were therefore plotted against propellant moduli, calculated from Wallace Hardness values. The curves were now nearly coincident; residual differences between the curves gave an order of merit for the propellants. From the fatigue point of view, the L.81 propellants studied were better than the L.77 propellants.

The High Temperature Strength of Plastic Propellants

CONFIDENTIAL

Two requests have been dealt with for information about the ability of plastic propellants to withstand short-time setback stresses at high temperatures. One concerned the ability of the Gosling XVA motor to withstand storage, and subsequent projection, at up to 30 g when the charge, or part of it, was at 70°C. The other concerned an R.A.R.D.E. project for a 6-inch motor with a short burning time (0.3 second) which reached accelerations of up to 200 g; the propellant (S.1007) was required to withstand the high shearing stresses involved at temperatures up to 50°C.

/Shear

Shear testing was carried out on both propellants at a range of temperatures and shear stresses. The techniques were similar to those used in earlier work on storage slump problems, but the range of breaking times was extended down to below one second. It was concluded that both propellants had sufficient short-time strength.

Biaxial Tensile Testing of Solid Propellants

CONFIDENTIAL

The biaxial tensile test has been developed further, and recent work has included a series of fatigue tests, a study of the effect of binder equivalence ratio on biaxial extensibility, and the testing of various experimental propellants. The ratio uniaxial/biaxial extensibility has been shown to correlate with the type of fracture obtained; cases where the biaxial extensibility tests put propellants in a different order from uniaxial tests have been shown to be due to differences in the type of failure.

2.1.5 Charge Defect Detection

Radiography: Image-Retaining Panel

UNCLASSIFIED

Preliminary tests have been carried out on an image-retaining panel recently developed by Thorn Electrical Industries. The panel consists of a thin steel backing plate coated with an electro-luminescent phosphor which is activated by an applied low d.c. voltage. X-rays, or visible light, then cause a visible image to be formed which persists whilst the d.c. voltage is applied. So far, the one plate tested has shown much lower sensitivity to X-rays in the 100 - 150 kV range than fine grain X-ray film, and a considerably more grainy image, but a fuller examination is planned with improved panels, in view of the simplicity of the method. The method should be suitable for inspecting small fuze assemblies etc. and D.I.Arm. has been informed of results.

2.1.6 Foreign Rocket Charges

CONFIDENTIAL

SNEB - 68-mm Aircraft Rocket

A visit was made to France to obtain details of the propellant in this rocket and observe the firing of motors which had been stored at 60°C. During discussions at Direction des Poudres it was revealed that the French have abandoned the use of lead acetylsalicylate as a platonising agent for cordite and are using lead stearate with carbon black to give a range of rates of burning. Two established propellants, TT.17 and TT.27, have burning rates of 0.67 and 1.06 inch/sec. at calorimetric levels of 800 and 920 cal/g. (W.L.) respectively but the pressure ranges of the plateaux have moved to considerably higher levels - above 2000 p.s.i. As would be expected with these ballistic additives, no change in rate of burning could be detected after storage for one and two months at 60°C as judged by the firing of a small number of motors. The star-centred charge for this motor is inhibited by cast polyester resin. Although this coating softens, due to the absorption of up to 16 per cent of nitroglycerine after 2 months at 60°C, it remains effective as an inhibitor and the thickness of coating (0.060 inch) is low enough to ensure that the loss of nitroglycerine from the charge has a negligible effect on performance.

/2.2

2.2 EXTRA MURAL ORDERS FOR BULK PROPELLANT AND EXPLOSIVES; CHARGES FOR TRIALS

Martin Baker Ejector Seat

CONFIDENTIAL

Supplies of charges in KU propellant have been continued and eight batches totalling 1100 lb. have been provided in this half-year. Supplies of the 1-inch size are now available from R.O.F., Bishopton. For U.S.A. requirements the rocket packs are to be fired at from +160° to -65°F (+74° to -54°C) and strand burning rates of KU have been measured at these temperatures. These show that the pressure at which the peak rate occurs rises with falling temperature from 2000 p.s.i. at 165°F to 2400 p.s.i. at -65°F. Recent firings of the rocket pack at -65°F have now shown considerable instability in burning, such as is usually found with platonised propellants burning at pressures below the peak. Martin Baker have been advised to operate at a chamber pressure of 2700 p.s.i. at ambient temperature to avoid unstable burning.

Application of Extruded Propellants to Service Requirements

CONFIDENTIAL

Experimental formulations have been devised and supplied for weapon development trials by various establishments:

(a) Ejector Release Units (R.A.R.D.E.)

A modified picrite composition has been supplied in 7-perforation granules to improve temperature corrections for this high temperature application (2 hours at 120°C).

(b) Cumulus Engine Starter Cartridge (R.A.R.D.E.)

An urgent requirement has arisen for the Cumulus Engine Starter for the TSR 2 owing to the failure of the hydraulic starter. A propellant burning at 0.15 inch/sec. at 1200 p.s.i. is required but has not yet been achieved in the four experimental compositions tried.

(c) Swingfire (R.P.E.)

It might be possible to use extruded charges for the dual-thrust Pointer rocket. Since there is very little experience of such charge designs with cordite, propellants AU and F.488/867, which are the nearest "standard" compositions for the required ballistics, have been supplied to R.P.E. for test firings to assess charge assembly problems.

(d) A.S. Mortar Mk.10 (Admiralty, U.W.R.E.)

Further proof stand tests are being conducted to determine the best size and shape of KU for optimum ballistic performance.

Plastic Propellant Production

CONFIDENTIAL

During this period tonnage quantities of propellant have been manufactured including lots for Rook, and inert-filled Goslings for packaging and inspection trials. A delivery of potassium perchlorate propellant (S.1050) has also been made to R.P.E; this is an alternative propellant for the CF.299 motor.

/K-rounds

K-rounds filled with S.1007 have been supplied in aid of the FFRI development programme and, to enable this motor to be filled, modifications to the Bigwood 20-ton press have begun.

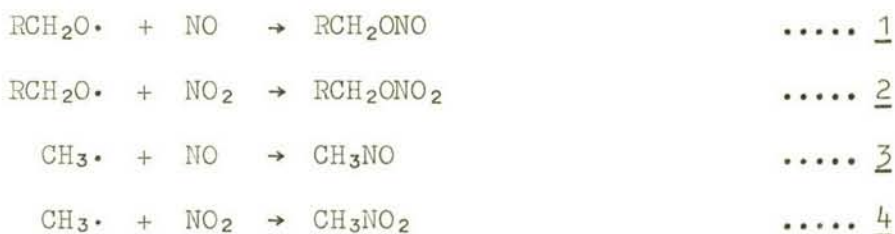
Some 55 2.75-inch GAR motors have been supplied for flight trials.

Following successful modifications to the venturi, the 5-inch diameter motor for Giant Viper has been fired over the temperature range 20° - 125°F (-7° to +52°C) and the results submitted to M.E.X.E. for comment.

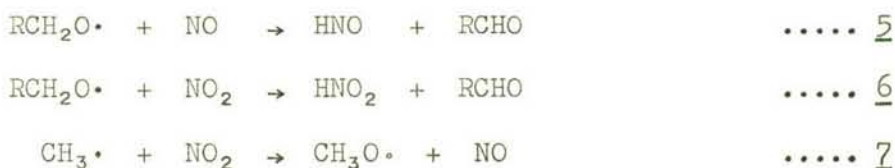
2.3 COMBUSTION AND ASSOCIATED PROBLEMS

The Gas-Phase Reactions of Nitric Oxide and Nitrogen Dioxide with Free Radicals UNCLASSIFIED

The importance of gas phase reactions between nitric oxide and nitrogen dioxide with free radicals in alkyl nitrate flames is well established, but little quantitative data is available. These reactions can be divided into two classes, combination:



and disproportionation:



Except for 3, for which the rate constant in the second order region is 10¹² mole⁻¹cm³sec⁻¹, no kinetic data are available.

Direct measurement of the rates of these individual reactions is normally difficult, if not impossible, but relative rates of combination to disproportionation can often be determined, so that provided the absolute rate of either is known, the other can be calculated. The rates of combination reactions can be calculated with fair accuracy provided the entropies (S) of radicals and adducts, and the frequency factors (A₋₁) of the dissociation reaction are known, reserving the relationship

$$X\cdot + Y\cdot \xrightleftharpoons[-1]{1} XY \qquad R\ln A_1/A_{-1} = \Delta S$$

/and

SECRET/DISCREET

and assuming that activation energies for radical combination reactions are zero.

Using known and calculated entropies, and experimental values for the frequency factors (A_1) of the dissociation reaction, the following combination rates have been determined:

<u>Reaction</u>	<u>A = k_1 (mole⁻¹cm³sec⁻¹)</u>
CH ₃ O. + NO	1.6 x 10 ⁹
CH ₃ O. + NO ₂	2 x 10 ¹¹
C ₂ H ₅ O. + NO	3 x 10 ¹⁰
C ₂ H ₅ O. + NO ₂	6 x 10 ¹⁰
i-C ₃ H ₇ O. + NO	3 x 10 ¹⁰

Allowing for the fact that these rates may be in error by a factor of ten, due to uncertainties in the entropies of the alkoxy radicals, they are all surprisingly low compared with the collision rate (10¹⁴ mole⁻¹cm³sec⁻¹). Also the reactivity of methoxyl radicals with nitric oxide appears to be much less than that of methyl radicals (measured rate 10¹² mole⁻¹cm³sec⁻¹).

From studies on the reaction of ethoxyl radicals with nitric oxide, k_1/k_5 appears to be about 3 at 135°C. Using the above calculated rate k_1 , this gives a value for k_5 of 1 x 10¹⁰ mole⁻¹cm³sec⁻¹.

From work on competitive reactions in the acetaldehyde/NO/NO₂ system at 90°C in which methyl radicals are formed, it appears that the absolute rates of the combination and disproportionation reactions of methyl radicals with nitrogen dioxide can be determined by relating them to the known rate of 3. Thus estimation of the yields of nitromethane, methyl nitrate, methyl nitrate and nitrogen from the reactions:

CH ₃ . + NO ₂ → CH ₃ NO ₂ <u>4</u>
CH ₃ . + NO ₂ → CH ₃ O. + NO <u>7</u>
CH ₃ O. + NO → CH ₃ ONO <u>8</u>
CH ₃ O. + NO ₂ → CH ₃ ONO ₂ <u>9</u>
CH ₃ . + NO → CH ₃ NO <u>3</u>
CH ₃ NO + 2NO → CH ₃ . + N ₂ + .NO ₃ <u>10</u>

enables k_4/k_7 and k_7/k_3 to be determined; results to date give values of k_4 of 1.2 x 10¹³ and k_7 of 1.8 x 10¹³ mole⁻¹cm³sec⁻¹. The latter is close to the known value for the oxidation of hydrogen atoms by nitrogen dioxide,

/whilst

whilst the former is faster than the methyl/nitric oxide reaction. The experimental value for k_9/k_8 is about two, whilst k_9/k_{41} is not less than fifty at 90°C.



The Effect of Silica on the Performance of Polyurethane Propellants

CONFIDENTIAL

Small additions of very fine silica to polyurethane propellants have been shown to increase the specific impulse by up to 2 per cent. Originally, this inert material was added to aluminised compositions in an attempt to reduce the agglomeration of molten aluminium at the burning surface so that combustion efficiency might be improved. Recent studies have shown, however, that, although silica has proved to be a valuable burning-rate catalyst, it does not improve the combustion of aluminium, or reduce the particle size of the aluminium oxide in the exhaust. Moreover, it has now been demonstrated that silica can apparently improve the specific impulse efficiency of non-aluminised polyurethane compositions. There is a strong indication that the explanation lies in a variation of specific impulse efficiency of the K-round with thrust level; fast-burning composition giving higher specific impulse efficiencies than those which burn slowly (heat loss corrections being taken into account). (See Table 2, p.15)

This effect of thrust level on K-round performance was also brought out in the recent study of the specific impulse efficiency of aluminised E.R.D.E. propellants (E.R.D.E. Report No. 13/R/63). No adequate explanation of the apparently low efficiency of polyurethane propellants, relative to plastic or double-base compositions, was revealed. In fact, the combustion efficiency of the aluminium was better and the alumina particle size was smaller for polyurethane compositions than for others. The higher specific impulse efficiencies of the plastic and double-base propellants could be correlated only with their higher rates of burning.

In order to understand the effectiveness of silica (usually a chemically inert material) as a burning rate catalyst a study has been made of its influence upon the degradation of the fuel and on the combustion of ammonium perchlorate. It was found that the rate of gasification of Daltorol containing 5 per cent SiO_2 at 400°C and 445°C was little different from the unadulterated polymer and that the burning of ammonium perchlorate (with, or without, small quantities of fuel) was strongly inhibited by 1 per cent SiO_2 . However, in a mixture of Daltorol and ammonium perchlorate it was shown that the rate of flame travel down binder/oxidiser interfaces was greatly accelerated by the presence of SiO_2 . The resulting increase in burning surface area could readily account for the observed increase in overall burning rate. The mechanism of this process is being studied and seems to be associated with the elimination of the viscous liquid intermediates, formed during the pyrolysis of the fuel, which impede flame spread.

/TABLE 2

TABLE 2

Non-aluminised Polyester Polyurethane Propellant	Burning Rate at 1000 p.s.i., inch/sec.	I_{sp} (measured) lb.f.sec/lb.	$E = \frac{100 I \text{ (measured)}}{I \text{ (theory)}}$ (uncorrected)	E (corrected for heat loss)
<u>I</u>				
<u>20 % Binder (no TEGN)</u>				
(a) with rate-reducing additive (1 % CaCO_3)	0.14	215.(3)	90.(1)	92.(7)
(b) no additive	0.23	227.(4)	94.(2)	96.(7)
(c) with rate-increasing additive (1 % SiO_2)	0.53	230.(9)	95.(9)	98.(3)
<u>II</u>				
<u>20 % Binder (containing 25 % TEGN)</u>				
(a) no additive	0.28	230.(9)	93.(8)	96.(5)
(b) with rate-increasing additive (1 % SiO_2)	0.67	233.(9)	95.(9)	98.(2)

Hydrogen/Oxygen Flames

UNCLASSIFIED

Hydrogen atom concentrations have been determined in low-pressure (30 - 100 mm Hg) fuel-rich hydrogen/oxygen/nitrogen flames over the temperature range $1225^\circ - 1375^\circ\text{K}$. The method involved mass-spectrometric analysis of samples extracted from the flames, to which a small proportion of D_2O had been added, in order to follow the increase up the flame of the ratio HD/H_2 . This increase is caused by the progress of the reaction:



(activation energy 21.1 kcal/mole). It is considered that the species H_2 , HD and H_2 are in equilibrium among themselves in the burnt gases of these flames, since the activation energy of an interchange such as



is only 6 - 7 kcal/mole.

/Current

Current results indicate that the excess of hydrogen atom concentration over its equilibrium value in these flames, is of the order 10^4 , and is a function only of temperature, not of flame composition, within a range of hydrogen concentration from about 20 to 120 per cent above stoichiometric; the excess diminishes with temperature increase. The results appear to interpolate well between results in the literature at 900° and at 1600° - 2400° K. Advantages of using low-pressure flames for this work are:

- (i) the importance of radical recombination (i.e. H with H or OH) which must be a three-body process in a homogeneous system, is reduced by lowering the pressure;
- (ii) the flames used are almost free; little heat is lost to the burner, and the temperatures are within 100 degK of the theoretical values.

2.4 EXTRUDED CORDITE

Improved Platonised Compositions

CONFIDENTIAL

For possible use in A/T. G.W., and also in a Norwegian sustainer motor, extruded propellants are being devised to simulate the ballistics of some recent higher energy C.D.B. formulations. These have a performance some 10 per cent higher than the well-established slow-burning platonised cordites such as TU. Experimental formulations using pyro nitrocellulose and variants on lead phthalate plus lead citrate as platonising agents have so far been tried, but although most of them are platonised at the correct rate, the pressure limits are around 400 p.s.i. rather than the required 1000 p.s.i. This difficulty in matching ballistics is largely due to the need for a higher nitrocellulose content, since the cordite charges will not be case-bonded and must be stronger than the C.D.B. Other modifications are being tested.

The work on lead compounds conducted over many years by the National Lead Corporation of America indicated that lead salicylamide and salicylaldehyde might give novel ballistics. In the first assessment in an extruded composition (950 cal/g.) lead salicylamide gave a plateau at 0.27 inch/sec. between 700 and 1100 p.s.i. and at about 1 inch/sec. between 4000 and 5000 p.s.i. A composition of this type with a double plateau may have applications as a boost/sustainer propellant for A/T. G.W. Lead salicylaldehyde gave a short plateau at 5000 p.s.i. at 1.45 inch/sec. Both compounds are being tested in other formulations.

2.5 CAST DOUBLE-BASE

Composite Modified C.D.B.

CONFIDENTIAL/DISCREET

After a long delay the remotely controlled facilities for incorporation and pressing with a controlled rate of rise of pressure are now installed and working smoothly; manufacture of composite-modified casting powders has restarted. Several batches of standard compositions (F.452/302, /368, /402 and /409) have been made to study the dependence of burning rate on ammonium perchlorate size, partly in support of the I.M.I. "Chow" motor, since I.C.I.,

/Ardeer

Ardeer have not achieved so high a rate as E.R.D.E. with F.452/302. Finely ground ammonium perchlorate ($S_0 = 10,000 \text{ cm}^2/\text{cm}^3$) has also been sent to Ardeer in a specially devised vacuum pack to prevent deterioration during transit and storage. Efforts to increase the burning rate of composite-modified propellants with potassium perchlorate catalyst (F.452/444) have given a high pressure exponent. Increasing the filler content from 45 to 55 per cent has given increased burning rates in K-rounds and this work is being extended.

Smokeless Boost Phase for Chow Motor

CONFIDENTIAL

To meet a Naval requirement of substantial smokelessness during the first half-second of burning, I.M.I. have proposed the Chow motor with a composite-modified main boost charge, coated with half-an-inch of a practically smokeless platonised propellant. In view of such novel design features, E.R.D.E. has investigated simplified dual-composition case-bonded motors to assess the problems involved. Modified 5-inch J-rounds with F.452/302/19 covered with a half-inch layer of ATN/D27/19 were cast without difficulties. The motors fired satisfactorily with the expected stepped-thrust curves.

Six-inch charges with the same dual composition have been temperature cycled, between -20° and 120°F (-29° to $+49^\circ\text{C}$) and composite 2-inch cubes stored at 80°C . Tensile specimens have also been tested after hot storage for up to 8 weeks at 120°F . Apart from slight weakening which can be explained by plasticiser inter-diffusion as a result of rather wide differences in composition, these tests have not revealed any unexpected trouble. The Chow charge geometry is rather complex, so I.M.I. storage trials with these motors and/or scale models are also necessary to clear the design.

Adhesives for Case-Bonding

CONFIDENTIAL

Collaboration has continued with I.C.I. and I.M.I. to lay down techniques and specifications for case-bonding adhesives and materials.

Storage trials have indicated that good bonding to epoxy resin fibre glass motor tubes can be obtained with propellants such as ATN, by use of a sprayed Formvar lacquer coating.

Hypalon/steel bonds formed with epoxide/polyamide and epoxide anhydride adhesives have been investigated. The absorption of NG from propellant by these adhesives is extremely low, of the order of 4 per cent, and bond strengths are high but some reservations exist concerning compatibility.

Graphiting of Casting Powder

RESTRICTED

To minimise electrostatic hazards during the filling of casting powder into moulds it is customary to dry-glaze the powder granules with about 0.05 per cent of graphite until the powder is electrically conducting. One or two casting powders, particularly AID types which are water-steeped in I.C.I. production, have been notoriously difficult to make electrically conducting. The problem of these "difficult" powders has now been solved by the use of a new type of air-floated graphite ($S_0 = 36,000 \text{ cm}^2/\text{cm}^3$) which is much finer than the Foliac grades ($S_0 = 18,000 \text{ cm}^2/\text{cm}^3$) currently used; specification amendments are proceeding.

/Slurry

Slurry Casting

CONFIDENTIAL

The size of the ball powder used has been found to affect burning rate; "Fluid ball powder" (E.R.D.E. or Olin) up to 0.003-inch size gives rates 0.1 inch/sec. lower than the up to 0.010-inch size.

Microscopic examination has shown that the TEGN liquid diffuses into the ball powder, during the cure, to form spheres of gel and, in the case of the 0.003 to 0.010-inch ball powder, the filler particles can be clearly seen to be packed in the interstices as a continuous phase.

Nitramines are being examined for ballistic effects coupled with high performance. RDX (control) and the di-ammonium and di-hydrazinium salts of ethylene dinitramine have been incorporated into laboratory-scale slurry castings for stability and sensitiveness tests before scaling-up the work or making conventional casting powders.

2.6 PLASTIC PROPELLANT

Potassium Perchlorate Propellants

CONFIDENTIAL

Following the promising results obtained with coarse potassium perchlorate, large-scale sources of this material have been investigated. Supplies were found to be available from the French and Swedish firms who manufacture ammonium perchlorate and an order was placed. The material received did not meet the provisional specification in respect of particle size. The sample taken had a specific surface of 1200 cm²/cm³ and gave a burning rate of 0.969 inch/sec. at 1000 p.s.i. (in propellant E.3941). This has confirmed that the variation of burning rate with specific surface is less with potassium perchlorate type propellants than with the ammonium perchlorate type. The burning rate is also higher for a given specific surface. Comparative results are shown in Table 3 below.

TABLE 3

Ammonium Perchlorate (E.3090)		Potassium Perchlorate (E.3941)	
Specific Surface, cm ² /cm ³	R _B at 1000 p.s.i.g., inch/sec.	Specific Surface, cm ² /cm ³	R _B at 1000 p.s.i.g., inch/sec.
400	0.583	500	0.805
2200	0.772	1200	0.969
5100	0.992	4200	1.073

/Effect

Effect of Impurities in Ammonium Perchlorate on Propellant Ballistics

CONFIDENTIAL

Work has continued on attempts to discover which impurities, if any, cause the differences in burning rates shown by supplies from different sources. The perchlorate supplied from Japan at present gives the fastest burning rates and this material has a high chromate content (up to 0.01 per cent). To investigate the effect of chromate content on the burning rates, ammonium perchlorate has been recrystallised in the presence of different concentrations of potassium dichromate and samples with chromate concentrations of up to 0.033 per cent have been obtained. The materials were sieved to give the same specific surface for each sample; batches of propellant E.3090 were incorporated and the strand burning rates determined. The burning rates decreased with increasing chromate concentration, the control with no chromate gave a burning rate of 0.799 inch/sec. at 1000 p.s.i.g. and the sample with 0.033 per cent of chromate gave 0.740 inch/sec. at 1000 p.s.i.g. The effect of other major impurities such as alkali metals and chlorates is now being investigated.

Aging of Plastic Propellants

CONFIDENTIAL

The effect of humidity on plastic propellant is being re-investigated. Previous experiments have shown that deterioration increased almost linearly with humidity, but recent results obtained by measurement of the water vapour permeability of samples of propellant, and the moisture pick-up of milled ammonium perchlorate, have not confirmed this effect. The permeability of propellant E.3090 has been shown to be negligible below about 80 per cent r.h.

The rate of penetration of moisture into propellant has also been measured by preparing thin "sandwiches" of E.3090 between microscope slides, storing these at constant temperature and humidity, and measuring the rate of advance of the interface between a blached area around the edge of the sandwich, where solution and recrystallisation of the ammonium perchlorate have taken place, and the unaffected propellant. This rate is also negligible below about 80 per cent r.h. although the rate measured at 100 per cent r.h. corresponds approximately to the rate of decrease of elongation.

2.7 POLYURETHANE PROPELLANT

2.7.1 Operation of the 1-ton Filling Plant

RESTRICTED

Phoenix Motor R. and D. Programme

This programme is proceeding at a slower pace than anticipated owing to motor design problems and has so far made small demands upon the N.550 filling facility.

/Mixing

Mixing and Filling Facility: Building N.550

CONFIDENTIAL

The facility is now completed, and five single-increment motor fillings have been carried out; four were successful, but one failed to cure. No satisfactory explanation has been found; efforts are being made to establish a quick test for checking "cure potential" before casting. Mixing time is about four hours for a 700-lb. batch, and mix viscosities have been encouragingly low. A new 3-inch dump valve has been designed and fitted to give the more positive control required for increment filling. All dispensing systems have been comprehensively tested and calibrated and perform satisfactorily. Numerous modifications to filling tools have been completed, and all are now satisfactory, as are the handling equipment, curing ovens and drying ovens. A comprehensive operating manual has been compiled.

Filling of Rocket Motors

CONFIDENTIAL

Some correlation has been obtained between K-round and strand burner figures and the pressures obtained in the 10-inch test motors; pressures in the larger motor can be predicted to ± 7 per cent and burning times to ± 10 per cent.

A 17-inch boost/sustainer motor was filled for a combined firing at R.P.E. but little information was obtained owing to early nozzle failure.

Firings of 10-inch and 24-inch sustainer motors have given anomalous pressure/time characteristics; the expected level trace has only been obtained in very early 10-inch firings and in the single 17-inch sustainer firing carried out so far. The effects of charge geometry and propellant properties are being explored fully before proceeding further with large motors, and three 10-inch sustainers have been filled with propellants of carefully graded burning rates between 0.18 and 0.24 inch/sec. at 300 p.s.i. as part of this investigation. The intermediate composition at 0.21 inch/sec. has given approximately the required pressure/time curve.

2.7.2 Other Work

Physical Properties of U.188 Propellants

CONFIDENTIAL

A constant strain apparatus is now being used to provide additional information concerning the relative merits of propellant compositions. In this test, the standard tensile specimen is stretched at a rate of 0.2 inch/min. until the required extension is obtained and then the behaviour of the specimen is noted over a period of one week. The temperature is maintained at 25°C and the humidity at less than 20 per cent r.h.

Generally, it has been found that there is an extension below which no apparent deterioration of the specimen occurs, then an extension range for which the specimen shows regional dewetting but does not fracture, and finally an extension above which the specimen breaks.

The advantage of this apparatus is that the test procedure more closely resembles the conditions found in a filled motor in which the curing and subsequent temperature changes have left permanent strains.

/Lowering

Lowering of the Cure Temperature of Polyester Polyurethane Propellants

CONFIDENTIAL

Two parallel approaches are being made; the use of an increased catalyst concentration and the use of more reactive isocyanates.

The concentrations of ferric acetylacetonate (FeAA) catalyst required to give the same rate of cure of U.188/L.77 propellant at temperatures below 60°C as has been achieved using 0.002 per cent FeAA at 60°C have been determined. These were 0.005, 0.015 and 0.03 per cent at 45°, 35° and 25°C respectively.

For the composition containing 0.005 per cent FeAA, reduction of the final processing temperature to 45°C gave a mix with a fluidity, 2 hours after the addition of TDI, similar to that normally achieved at 60°C (0.002 per cent FeAA). For compositions containing 0.015 and 0.02 per cent FeAA, final processing temperatures of 35° and 25°C respectively gave mixes with about twice the usual viscosity.

Propellant physical properties were unaffected by the reductions in cure temperature and measured densities were equal to the theoretical value. The storage stabilities of propellants containing up to 0.04 per cent FeAA are being determined.

A laboratory-scale preparation, described on p. 4, has provided 80 g. of 3-nitrazapentane-1,5-di-isocyanate (NPDI) for assessment as a replacement for TDI in polyurethane propellants. The results obtained from the two batches of U.188/L.77 propellant prepared using this di-isocyanate have shown a significant increase in cure rate over that obtained with TDI. For example, full cure was achieved in five days at 35°C without the addition of FeAA. An adequate 'pot-life' was obtained by reducing the final processing temperature to 45°C.

NDPI has several advantages over TDI and in addition the use of a more reactive isocyanate is preferable to the use of an increased catalyst concentration, as the stability of the finished product will probably be better.

/3

3.2 MEASUREMENT OF THERMAL PROPERTIES

Nucleate Boiling and High Heat Flux Supercritical Heat Transfer

UNCLASSIFIED

The apparatus has been modified to allow higher flow rates to be attained. The highest flow rate of 2.3 lb/sec., so far obtained, (corresponding to fluid velocity of 22 ft/sec. in the test channel) may be improved upon.

Experiments are in progress to determine the optimum conditions of lighting to obtain high-speed ciné photographs of nucleate boiling and supercritical convective heat transfer from the external surface of a heated tube. By using an arrangement whereby heating was confined to 1/16-inch wide metal strip along the top surface of a 1/4-inch diameter rod of non-conducting material, a ciné film showing nucleate boiling and partial film boiling in close proximity on the heating surface has been obtained.

Detailed results are given in E.R.D.E. Report No. 5/R/63.

The Hydrogen/Oxygen Rocket

Heat Transfer Studies at 10 atm Combustion Pressure

UNCLASSIFIED

The evaluation of the radiative heat flux from measurements of the total heat flux has been completed. For the two injector configurations employed in these tests (a showerhead and a vortex type) the observed radiative heat flux for propellant mixture ratios between 60 per cent oxygen deficiency and 60 per cent oxygen excess was identical within the experimental scatter of ± 10 per cent. This result confirms the usefulness and reliability of the experimental method employed. The radiative heat flux in the combustion chamber increased from a value of about 18 cal/cm²sec. at 60 per cent oxygen deficiency to a maximum of 33 cal/cm²sec. around the stoichiometric point, and fell off less steeply with increasing oxygen excess to a value of 28 cal/cm²sec. at 60 per cent oxygen excess.

The high radiative heat flux for this propellant combination might well present a serious problem to the development of high pressure hydrogen/oxygen rockets.

High Pressure Gas Radiation

UNCLASSIFIED

In connection with the extension of the experimental study of radiation to higher gas pressures, a motor-driven, variable-throat, water-cooled plug nozzle has been developed.

The use of this nozzle will allow a continuous change of nozzle throat area and thus permit a rapid and continuous variation of propellant flux at constant combustion pressure and propellant mixture ratio. This is, of course, one of the basic requirements for applying the technique previously used for determining the radiative and convective components of the total heat flux.

/The

The Thermal Conductivity of Liquid and Gaseous Ammonia

UNCLASSIFIED

The thermal conductivity of ammonia in the liquid-like fluid states is a unique function of density. A correlation equation of the experimental thermal conductivity data and published density values has been obtained by the Mathematical Dept., R.A.E., Farnborough. A least-square analysis up to degree 6 was applied, but in view of the probable error of up to 1½ per cent for both quantities, a second degree equation appeared to be of adequate accuracy. The equation:

$$k \times 10^4 = 8.695 - 27.015\rho + 52.591\rho^2,$$

has been experimentally verified in the range 507 - 804 Amagat, but may be extended without serious loss of accuracy to predict the thermal conductivity of liquid ammonia at pressures up to 1000 atm (883 Amagat).

A comparison of the calculated thermal conductivity of liquid ammonia at the density of solid ammonia (1037 Amagat) with the experimental value of thermal conductivity of solid ammonia (Eucken and Englert 1938), showed that the proposed correlation equation might hold with reasonable accuracy for the entire dense fluid range (500 - 1040 Amagat).

Evaluation of experimental values and comparison with previous work in the low-density gas phase suggested that a small heat loss, hitherto unimportant, was influencing the results when low heat fluxes had to be used. A careful analysis of possible paths of non-radial heat flow from the cell heater allowed a suitable correction term to be evaluated. With this correction applied, excellent agreement - better than 1 per cent - was obtained with the gas phase data of several previous observers.

/4

4.1 IMPROVEMENTS TO MEET SERVICE REQUIREMENTS

Ballistic Stability of Picrite Cordites

CONFIDENTIAL

For some years the loss in vivacity of picrite cordites on storage at temperatures above 120°F (49°C) has been thought to be due to the presence of the picrite/carbamite complex but there has been no experimental confirmation. More recently the unexpected fall in ballistics of a standard lot of MNLF.2P was considered by some to be due to the presence of dibutyl phthalate or even the potassium sulphate. An accelerated climatic trial lasting 6 months at 160°F (71°C) has been conducted using modified guncotton compositions containing 2-N.D.P.A., dibutyl phthalate, dioctyl phthalate and potassium sulphate. The Closed Vessel firings indicated:

(a) Absence of the picrite/carbamite complex gave much improved ballistic stability and the changes were well under one per cent even under these extreme storage conditions.

(b) The scatter of results did not enable precise comparisons to be made but it was indicated that the size of picrite, presence of either dibutyl or dioctyl phthalate or potassium sulphate had no large effects.

Temperature Coefficients of Picrite Cordite

CONFIDENTIAL

Attempts to achieve low temperature coefficients in the 105-mm tank gun have been confined to the NQ composition (880 cal/g.), since R.A.R.D.E. considered that there would be difficulty in obtaining the required performance from cooler propellants such as F.527/224 (690 cal/g.) which had given a very small temperature coefficient in the 40-mm L.70 gun. This is now being re-examined in view of Dutch claims that the required ballistics can be achieved at 760 cal/g.

A cool picrite composition (690 cal/g.) as 19-hole granules, although of too small a ballistic size for this gun, showed a promising improvement in temperature coefficient compared with NQ propellant. A comprehensive investigation at a range of calorimetric values is being planned with R.A.R.D.E., as D.G. of A. requires a propellant with low temperature dependence for the new Chieftain gun.

A Closed Vessel investigation has been conducted to determine how erosive burning depends upon the diameter and length of the perforations in multi-perforated granules. A batch of NQ dough was pressed through a number of 7-pin dies to give batches of granular MT7 propellant with perforation diameters from 0.004 to 0.024 inch. For each perforation size the cut lengths of the granules ranged from about 18 to 50 times the perforation diameter. The Closed Vessel transients showed clear evidence of erosive burning in those batches with perforation diameters of 0.014 inch or less, while the effect of granule length was small. The persistence of the effects up to 0.014-inch diameter is noteworthy as much less difficulty will be experienced in bulk production than with the 0.008-inch perforations originally thought necessary.

/Combustible

Combustible Cartridge Cases

CONFIDENTIAL

Modifications to reduce handling problems have been introduced into the experimental manufacture of cylindrical cases for the 84-mm gun. Collaboration with R.O.F., Bishopton has continued and experimental manufacture appears on a satisfactory basis.

Attempts to reduce the amount of nitroglycerine absorption on high temperature storage, by cross-linking the Formvar resin or coating with methyl cellulose have not been successful.

At the suggestion of R.A.R.D.E.(P2) a technique was worked out for making cases containing about 10 per cent titanium dioxide uniformly distributed throughout the case wall, as an aid to reducing barrel erosion. There are indications that such cases made from pyro NC/Iggesund Kraft, 2/1 ratio, have a tensile strength of about 1700 p.s.i. compared with a more usual level of 1300/1500 p.s.i. for the plain case.

Experimental manufacture of the tapered cases for the 105-mm gun was started and a successful procedure established for preliminary firing trials. As an aid to processing these cases, seamless tubular gauze of cotton or rayon was slipped over the dried preforms. The gauze can be left bonded to the case and may assist in delaying cook-off in a hot barrel; if no advantage accrues an alternative grade of gauze can be selected so that it can be stripped from the case.

/5

5.1 SAFETY CERTIFICATE TESTS; HAZARD APPRAISAL; AD HOC TRIALS

Hazards in Manufacture of Elastic Priming Composition

RESTRICTED

Tests have been carried out to investigate the effect of ignition during incorporation and extrusion of IT26B, a mixture of potassium perchlorate, Thiokol, boron, plasticising and curing agents.

(a) Incorporation

If boron is added at too great a rate or the incorporation time is shortened, a crumbly mixture is obtained, and it is thought that this is the most dangerous type of mix. A 1-litre squat stainless steel beaker, fitted with a heavy brass rim, was filled at about half capacity with a crumbly mix of IT26B (750 g.), embedding a 1 g. SR371C igniter near the bottom. A 1/8-inch stainless steel lid was fitted and held in place by three Terry clips. After firing the igniter the beaker, lid and rim were recovered intact, though bent. Burning composition was scattered around the walls of the firing point. It was clear that a pressure burst had taken place.

(b) Extrusion

R.O.F. Glascoed provided a mock-up of an extruder barrel. It consisted of a hollow cylinder 10 inches deep, 3 inches internal diameter; except for the top, the wall thickness was 1/2 inch. It was closed at the bottom except for a small hole, centrally placed, to represent a die. The top of the cylinder was thicker to accommodate eight screws to hold the steel lid, 4 1/2 inches diameter, 1/2 inch thick. The screws were reduced to yield at an internal pressure of 3000 p.s.i., the working pressure of the extruder. An electric heater was wound around the outside of the cylinder.

IT26B (2250 g.) was filled into the cylinder, embedding a 1 g. SR371C igniter in the middle of the charge, with the leads emerging via the die hole. The pot was heated until the cylinder walls reached a temperature of 100°C. After ignition, the cylinder and lid were both recovered intact. All the screws had sheared and the heads were recovered. Burning composition was scattered around the walls of the firing point. Again it was clear that a pressure burst had taken place. These trials show that should an ignition occur with the above quantities of IT26B during incorporation or extrusion, a pressure burst only will be obtained.

Contamination of HTP by Refrigerating Agents

UNCLASSIFIED

In response to a request by Bristol Siddeley Engines Ltd., friction and impact tests have been carried out to assess the hazard should HTP accidentally mix with refrigerating agents leaking from a small refrigerating plant used to cool the hydrogen peroxide. Arcton 11, (trichlorofluoromethane, b.p. 23°C) and Arcton 113, (tetrachlorodifluoroethane, b.p. approx. 90°C) were chosen for the tests, since difluorodichloromethane, the usual agent, would have been too difficult to handle, its b.p. being -30°C.

/Mallet

Mallet friction tests were carried out with stainless steel tools, and impact tests were carried out using the cup and plunger arrangement in the Rotter machine.

The following were tested:

1. 87 per cent HTP at ambient temperature,
2. 87 per cent HTP (50 per cent) and Arcton 113 (50 per cent) at ambient temperature,
3. 87 per cent HTP at -10°C (impact only),
4. 87 per cent HTP (50 per cent) and Arcton 11 (50 per cent) at -10°C (impact - friction at ambient temperature).

From the results obtained it appears that Arcton 113 and Arcton 11 have a slight desensitising effect on HTP. It is highly probable that difluoro-dichloromethane would behave similarly, especially as it is known that in fully halogenated materials the reactivity with peroxide decreases with increasing fluorine content. Moreover it would evaporate rapidly in the refrigerator if a leak occurred.

Thus an accidental leak of refrigerating agents into HTP is not likely to present a greater hazard than HTP itself.

Categorisation of Propellants

RESTRICTED

Two new tests have been devised for the purpose of assessing the consequences of an accidental ignition. They are (a) the Bonfire Test, and (b) the Large Sealed Vessel Test. There are two versions of the latter whereby the contents are ignited either by an igniter or by external heating.

(a) The Bonfire Test

Ten pounds of propellant contained in a polythene bag are put inside a wooden box, internal dimensions 12 x 7 x $5\frac{1}{2}$ inches, which is placed centrally on a stack of 150 lb. dried deal made up of pieces, 4 feet x 1 inch x 1 inch. The base of the stack is 4 feet square. A rag lightly soaked in paraffin is placed on the windward side and ignited by a 3 g. SR371C igniter. Note is made of (i) the time elapsing between flame reaching the box and ignition of its contents, (ii) the length of time of the major conflagration, and (iii) the width, height and radius of the flame.

(b) The Large Sealed Vessel Test

The vessels for both versions are made from 3-inch I.D. mild steel tube of $\frac{3}{8}$ -inch wall thickness, and can contain $2\frac{1}{2}$ to 3 lb. of propellant depending upon the bulk density. A plug, 1 inch thick, is welded inside one end and the tube peened over. A similar 1-inch plug, containing a hole with a tapered screw thread, is welded inside the other end and also peened over. The vessel is filled via the tapered hole and sealed with a screw plug. The igniter version has provision for placing the igniter within the material under test. The heated version has a thermocouple

/strapped

strapped to the outside before the Nichrome heating element is wrapped around, and another thermocouple is placed in a tube running down the inside of the vessel and touching the inner wall. The heater supply is adjusted to give a 5 degC/min. rate of heating as measured by the outer thermocouple. The results obtained may be divided into four types - pressure burst, low order explosion, explosion, and detonation.

The Bonfire Test, together with the Bickford Fuze Ignition Test and the Train Test, do not specifically provide evidence which will enable a decision to be made between Safety Distance Category Y and ZZ risks, although in each case a positive result can mean that the material in question should be graded ZZ. The Large Sealed Vessel Test, however, is intended to provide such evidence. On the basis of a limited number of trials it is suggested that materials which, in this test, give detonation or explosion with either form of initiation (irrespective of the other result) or give low order explosion with both, shall be classified as ZZ. Materials which give pressure bursts with both forms of ignition shall be classified as Y. Materials which give a pressure burst with one form of initiation and a low order explosion with the other, should be classified Y if they are relatively insensitive to spark and friction, and ZZ if they are sensitive to spark and friction. A material is insensitive to spark if it fails to ignite in the case of ignition (Bickford Fuze) test, and if its electrostatic energy is greater than 0.02 joule. It is insensitive to friction if the data for friction are nil on softwood, nil on hardwood, but can be 100 per cent on Yorkstone.

Electrostatic Hazards with Stores and Packaging Materials

CONFIDENTIAL

(a) Polythene Containers

Further samples of conductive polythene containers with 25, 30 and 35 per cent carbon black have been tested (see TR.2/62). Containers for 81-mm ammunition and X2E2 detonator boxes have been made with 25 per cent carbon black, and better conduction has been found in the former than in the latter. Recent samples of X2E2 detonator boxes with the same carbon content but of a different composition as regards the other constituents, have given even lower resistances. These results confirm the previous ones indicating that 25 - 30 per cent carbon black will cover all antistatic requirements for use with electrically initiated stores.

(b) Hypalon Coated Nylon Shelter

CONFIDENTIAL

The hypalon coated nylon shelter for servicing the VR.725 weapon system (containing F.53 igniters) was considered to give rise to some electrostatic risk under conditions of low humidity. This is caused by personnel brushing their clothes against it, and a drill procedure for earthing them has been proposed.

(c) Polystyrene Foam

RESTRICTED

Polystyrene foam, sandwiched between the primary and outer containers for V.T. fuzes, has been assessed for electrostatic charging. Potentials of up to several hundred volts have been observed but were not thought to be hazardous since the construction of the fuze and the primary container offered sufficient protection to the igniter inside.

/Effect

Effect of Humidity on Static Electrification

UNCLASSIFIED

An investigation has been started on the effect of humidity on static electrification and electrical resistance, to decide whether these properties are determined more by the actual vapour pressure of water than by the relative humidity. At present - minimum r.h. of 65 per cent is stipulated for second degree precautions at any temperature above 65°F (18°C) and, for example, it would be very helpful if a relative humidity of less than 65 per cent could be used when the temperature is say 75°F (24°C) or more. The first part of the investigation has been a study of the electrical resistance of various fabrics, on which their electrostatic properties depend, at relative humidities varying from 30 to 80 per cent over a temperature range of 15° to 30°C (59° to 86°F). Allowing for the difference in absorption of moisture with temperature, the results so far show that the same resistance is obtained when simultaneously the r.h. is lowered and the temperature is raised, suggesting that the actual vapour pressure is of more importance than the relative humidity.

5.3 FUNCTIONING AND DETONATION STUDIESEquation of State Measurements on Explosives

UNCLASSIFIED

For reasons reported previously, the wedge technique for determining the shock Hugoniot of unreacted RDX/TNT explosive has been replaced by a technique in which pairs of argon-filled gap assemblies are used in conjunction with a high-speed streak camera to time the passage of shock waves or free surfaces over accurately measured distances. Velocities averaged over a distance of approximately 1 mm are obtained in this way, whereas the wedge technique records velocities continuously.

A flat shock wave is passed through an accurately machined brass attenuator plate in which are milled two parallel, flat-bottomed grooves of 0.025 and 0.050 inch depth. These grooves are 0.25 inch wide and 0.5 inch apart and a thin wafer of the explosive under investigation is mounted on the free surface of the brass plate between the grooves. Various thicknesses of explosive up to 0.150 inch have been used, the wafers being machined from RDX/TNT of constant composition and density. Argon gap assemblies in the grooves and on the surfaces of the brass plate and explosive wafer enable shock velocities to be measured, whilst other gap assemblies stood off from these surfaces by accurately known distances are used for free surface velocity measurements.

First results exhibit a greater scatter than anticipated, with inconsistencies between shot and shot and between measurements derived from a single shot. The nature of these inconsistencies indicated that inaccuracies in charge assembly may be responsible. However, the results show an approximately linear dependence of the brass shock velocity and free surface velocity on plate thickness. The measured shock and free surface velocities for the RDX/TNT wafers of various thicknesses suggest a continuous acceleration of the shock wave which enters the explosive. These preliminary results are in conflict with those from the wedge experiments, which indicated an induction period during which the initial shock velocity remains sensibly constant, followed by a fairly rapid acceleration and the onset of detonation.

/Detonation

Detonation Temperatures in Condensed Explosives

UNCLASSIFIED

A time-resolved electro-optical method is being used to determine the spectral distribution of energy radiated from a detonation wave. Comparison with the distribution from a standard source enables the temperature to be estimated, provided the detonation radiation is "grey body".

The previously reported poor signal/noise ratio at the photomultiplier outputs has now largely been overcome by increasing the effective aperture of the optical lens system and by replacing the laminated safety glass windows in the firing chamber by 1-inch Perspex, which has better optical transmission properties.

The time constant of each photomultiplier output has been improved considerably to approximately 13 nanoseconds by the addition of a cathode follower stage. Cathode follower circuits which should give even smaller time constants are being designed and tested. With a very fast oscilloscope, such as the 100 Mc. Tektronix 585 recently purchased, the overall time constant is sufficiently small to enable a study to be made of the initiation process and the transition to steady state detonation.

A considerable number of experimental determinations of the detonation temperature of nitromethane has now been made. The results are summarised in the following table.

TABLE 4

Expt. No.	Emissivity of Products, ϵ	Detonation Temperature, T	Recalculated T, Assuming $\epsilon = 1$
		$^{\circ}\text{K}$	$^{\circ}\text{K}$
1	1.67	3305	3515
2	1.49	3362	3528
3	1.88	3365	3591
4	1.29	3431	3547
5	1.75	3300	3539
6	2.61	3209	3618
7	0.74	3737	3582
8	0.84	3782	3666
9	2.39	3223	3614

It is seen that the apparent detonation product emissivity is variable and mostly greater than unity. There is considerable chromatic aberration in the Aero-Ektar lens system in use and this can lead to incorrect calibration of the apparatus using a standard lamp.

/Consequently

Consequently the measured ratio of intensities of radiation from the detonation and standard lamp and the derived emissivity can be in error and will depend on the value of the wavelength of radiation focussed on the entrance slit of the spectrometer. For this reason it is intended to eliminate chromatic aberration by replacing the lenses by a reflective system; preliminary tests are in progress.

If the detonation temperatures are recalculated assuming an emissivity of unity then reasonably consistent values are seen to be obtained.

Thermal Decomposition of Solids

UNCLASSIFIED

(a) p-Nitroperbenzoic Acid

Reproducibility of experiments on the decomposition of p-nitroperbenzoic acid has been improved by carefully storing in the dark a small batch of freshly prepared material and using it in a series of experiments before it has time to "age". In this way, the value for the activation energy has been determined as 37.7 ± 0.3 kcal/mole. Addition of impurity acids such as benzoic, p-toluic, p-chlorobenzoic and p-hydroxybenzoic, affect the decomposition. The high melting acids catalyse the reaction, the rate constant k in the expression $\alpha = kt^n$ (α is the fraction decomposed in t sec.) being proportional to the weight of added impurity. Benzoic acid inhibits the reaction, presumably being volatile enough to compete with the p-nitroperbenzoic acid for the active sites on the surface of the p-nitrobenzoic acid crystals.

(b) Alkali Metal p-Nitroperbenzoates

Since the decomposition of p-nitroperbenzoic acid has been shown to be a gas/solid reaction, an investigation into the alkali metal salts was made in the hope that their decomposition would involve true solid reactions. Lithium, sodium and potassium p-nitroperbenzoates were prepared in yields of greater than 70 per cent and between 70 and 80 per cent purity by a reaction of saturated aqueous hydroxide with an ether solution of p-nitroperbenzoic acid, the resulting salt being precipitated from solution, collected, washed with alcohol and dried. All are unstable, evolving oxygen at 0°C . Attempts to prepare the barium salt were unsuccessful.

(c) m-Nitroperbenzoic Acid

m-Nitroperbenzoic acid has been prepared in 40 per cent yield and 98 per cent purity. The gaseous products of decomposition are identical with those obtained from p-nitroperbenzoic acid, and the solid product is m-nitrobenzoic acid. The course of the reaction follows the usual sigmoid curve. At 66.5°C the decomposition proceeds without melting taking place; at higher temperatures a liquid phase is formed. This liquid phase solidifies as the decomposition nears completion i.e. when α is greater than 0.9. No break is observed (at the higher temperatures) in the continuity of the decomposition/time curve at the point of the solid to liquid phase change. It seems that the decomposition is not of the gas/solid type exhibited by p-nitroperbenzoic acid.

/The

The Thermal Stability of Secondary Explosives

UNCLASSIFIED

Attempts have been made to use kinetic parameters obtained from the isothermal decomposition of explosives to predict their sensitiveness in impact tests. Although it has been frequently stated that the initiation of explosion by impact is due to rapid exothermic decomposition in "hot-spots", previous attempts to bridge the gap between the comparatively low temperatures of isothermal studies and the high-temperature adiabatic conditions of "hot-spots" has been unconvincing.

Some success has been achieved by using G.B. Cook's solution of the heat balance equation for an infinite slab of explosive in contact with an inert planar heat source at constant temperature. It is thought that this model approximates to the conditions of an impact test, on sandpaper. Instead of assuming, as in previous calculations, that the "hot-spot" is formed in the explosive itself, the quartz particle is taken as the inert heat source or "hot-spot", and the time taken for explosion to build up in the surrounding material calculated. Since in the impact test the temperature of the "hot-spot" is high, explosion occurs very close to the surface of the quartz, and the conditions of the equation approximately hold. The temperature at which the calculated explosion time equals 250 μ sec. (the order of magnitude of the time of contact of the tools in the impact test) has been calculated for a variety of secondary explosives and plotted against the sensitiveness of the material on the N.O.L. sandpaper test. A straight line was obtained which was more striking than any previous correlation of which we are aware.

The appropriate kinetic and sensitiveness data are available for only a limited number of explosives, viz. NG, PETN, RDX, HMX, EDNA, tetryl, TNT and ammonium nitrate. To add to this list, a programme of thermal decomposition work has been started. Trinitrobenzoic acid has been found to decompose with a frequency factor of $10^{18.8}$ and an activation energy of 50.2 kcal. Mass spectrometric analysis of decomposition products showed the reaction to be mainly a decarboxylation and hence the heat of decomposition (calculated as 6.4 kcal) is unusually low for an explosive. Using these parameters the temperature at which trinitrobenzoic acid explodes after 250 μ sec. was calculated and correlated against its measured impact sensitiveness. The resulting point fell very close to the line previously obtained.

Picric acid has also been studied. The activation energy is 32.4 kcal and frequency factor $10^{11.3}$. Since decomposition products have not yet been analysed the heat of decomposition is not known, and correlation with sensitiveness cannot yet be made.

The Thermal Stability of Primary Explosives

UNCLASSIFIED

The isothermal parameters of the previous section were obtained from decompositions in the liquid state. Primary explosives decompose without melting, and the complicated and irreproducible nature of this decomposition makes extrapolation to high temperatures of doubtful value. A deeper knowledge of the process leading to decomposition must be obtained before any correlation with sensitiveness can be attempted.

/Apparatus

SECRET/DISCREET

Apparatus has been set up to study the thermal decomposition of azides, and a few runs on potassium azide have been carried out. These have been highly irreproducible, and the factors causing this are being investigated.

Cells have also been constructed to study the ultraviolet absorption spectra and the photoconductivity of azide crystals and other primary explosives. The combination of these techniques will measure the energy required to transfer an electron into the conduction band of the crystal, and several investigators have suggested that this is the rate-determining step in azide decomposition. Spectra of alkali and alkaline earth azides have been recorded, but both of these techniques are still in the development stage.

/6

SECRET/DISCREET

Lead Trinitrophloroglucinate

RESTRICTED

The study of the preparation and properties of this explosive has continued, especially with respect to the isolation of the two stable polymorphs of the normal salt. Using trinitrophloroglucinol made from phloroglucinol obtained from America the A type ($\Delta = 3.93$) has been reproduced successfully on the $\frac{1}{2}$ -lb. scale. The process consists of the addition of lead acetate solution to a stirred solution of the magnesium salt, pH = 5.8, at 70°C. At higher temperatures or on prolonged heating the B type ($\Delta = 3.97$) tends to form; at lower pH a hydrated lead salt separates out. Magnesium trinitrophloroglucinate solution of pH = 5.8 is stable on storage up to about 10 days but at pH = 4.0 breakdown of the trinitrophloroglucinol structure occurs rapidly with evolution of gas and precipitation of magnesium oxalate; this is being investigated.

Other Compositions

CONFIDENTIAL

The results of R.A.E. trials on fuseheads dipped R.D.1349 with ethyl cellulose binder show no desensitisation after 2 weeks at 150°C or two 8-hour cycles at 180°C and no reduction in peak gas pressure after 4 weeks at 120°C.

The preparation of R.D.1358 (lead 4,6-dinitroresorcinate) for fuseheads has been developed to larger scale giving reproducible $\frac{1}{2}$ -lb. batches. In response to a request for a free running material of similar explosive properties a granular form has been made on laboratory scale and supplied for test.

The pressure/time and work output characteristics of the new compositions are being studied for their applications to explosive motors. The methods of manufacture of R.D.1340, R.D.1349 and R.D.1358 have been demonstrated at E.R.D.E. to representatives from the Research and Development Department of I.C.I. (Nobel Division).

The effect of heat on cerium/magnesium alloy both untreated and desensitised with ethyl cellulose, also in mixtures and co-precipitated with R.D.1340, has been examined using the thermogravimetric balance. Co-precipitation gives greatest protection against oxidation (loss 0.1 per cent), the untreated alloy gaining over 2 per cent at 2degC/min. rise to 170°C.

Modification of Initiators by Co-precipitation with Boron

CONFIDENTIAL

The previous Technical Report described how electrostatic spark sensitiveness could be markedly reduced by co-precipitating the explosive with finely divided boron. This work has continued with the objects of studying possible mechanisms and of providing compositions to meet technical requirements.

/A

SECRET/DISCREET

A new method for preparing normal lead styphnate of improved properties has been worked out on small plant scale. Lead nitrate solution is added to a slurry of magnesium styphnate containing boron and polyvinyl alcohol at 45°C. The purpose of the polyvinyl alcohol is to suppress the beta polymorph which otherwise forms freely at this temperature. The product consists of uniform small crystals, containing 10 per cent boron, suitable for percussion or electric conducting compositions, with a threshold energy for ignition of 1000 ergs (partials), metal/metal electrodes. Preliminary tests by R.A.R.D.E. of experimental N.8 igniters containing this lead styphnate show that they are significantly less sensitive and may assist development of stores where radio hazards must be overcome.

Co-precipitation of monobasic lead styphnate with boron is more complicated. Thus additions of boron of 5 per cent cause change from beta to alpha polymorph although 10 per cent does not. With normal lead styphnate desensitisation is evident for both metal/metal and rubber/metal electrode systems of test; with the monobasic salt marked desensitisation on metal/metal test is not reproduced on rubber/metal.

Normal lead 2,4-dinitroresorcinate has been co-precipitated with boron on semi-technical scale and this product, together with lead styphnate/boron is being examined as a component of tetrazene-free stab sensitive compositions of improved thermal stability.

Barium styphnate co-precipitated with boron has been supplied to I.C.I. for test as a flash dip for fuseheads - priming dip R.D.1349 in ethyl cellulose. The results show that the composition is effective for providing small, intense hot spots with igniting power comparable to that of cerium/magnesium alloy. The new composition offers advantages in manufacture, safety and thermal stability. On the thermogravimetric balance there is no change in weight up to 190°C at 2degC/min. rise.

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7

NON-METALLIC MATERIALS

7.1 POLYMERIC TYPES

7.1.1 Thermosetting Plastics

Mechanism of Formation of Polyester Resins

UNCLASSIFIED

The esterification of adipic and maleic acids with ethylene glycols has been followed kinetically by determination of the water evolved. The reaction rates are approximately third order but the rate of esterification in the early part of the reaction has been found to be less than that occurring in the later part of the esterification; this phenomenon has previously been reported by Flory and Pope for similar systems.

The Ingold-Day theory for esterification in solution in aqueous or alcoholic media suggests the formation of an alcohol-acid transition state. The idea that this transition state is an actual molecule with a finite life is put forward as an explanation of the results and support for this is derived both from the present work and from the literature. A draft report is in preparation.

7.1.2 Thermoplastics

Impact Experiments on Polymers

UNCLASSIFIED

In the search for a simple method of measuring the dynamic modulus of elasticity in compression, experiments on the longitudinal impact of a steel sphere on the flat end of a 1-inch diameter Perspex rod have been continued. It is necessary to measure the maximum contact area produced during impact and this has been determined by using an ink consisting of vaseline compounded with a yellow filler. A thin smear of the ink on the impactor, radius R, leaves a well-defined ink spot on the specimen after impact.

In all cases the diameter, $2r$, of the ink spot is less than the contact-area diameter calculated using the Hertz theory represented by the relationship $r^5 = AR^5h$ where A is a constant and h the height of fall of the impactor. The results, however, were best described by the empirical relationship $r^6 = BR^9/2h$ where B is a constant ($B = 6.07 \times 10^{-8} \text{ cm}^2$).

In all cases it was found that the contact-area diameter was only independent of the length of rod above a certain critical rod length. Experiments on steel rods have led to similar conclusions. The impact of two rods is being investigated using the same method.

The results of earlier work were given at a Symposium, the proceedings of which are now published in Society of Chemical Industry Monograph No. 17, 1963, with the title "Techniques of Polymer Science".

/Sound

Sound Velocity Method of Measuring the Bulk Modulus of Elasticity of a Polymer

UNCLASSIFIED

The ultrasonic interferometer has been built and the velocity of sound in water measured over a temperature range of 20° to 80°C at 1.5 Mc/sec. Comparison with similar results in the literature showed that the apparatus was functioning satisfactorily.

Attempts have been made to measure the sound velocity in liquid suspensions of Perspex powder. Difficulties have arisen with regard to a suitable liquid. At present it seems that the best medium is a silicone oil which gives stable suspensions by virtue of its viscosity. The oil does not appear to swell the polymers.

Metal-Polymer Impact: Generation of Electrical Charge

UNCLASSIFIED

Experiments have suggested that greater accuracy and reproducibility of results would be possible by studying the electrical effects produced when the flat end of a thin-walled cylinder is pressed against a flat polymer surface by a dynamic pressure. A pressure bar system using this method has been constructed and a technique devised for measuring the electrical charge transferred from metal to polymer during a dynamic compression.

Dynamic Flexure of Thin Plates of Plastics

UNCLASSIFIED

The study of the dynamic flexure of thin plates has been continued with experiments on the forced vibration of centrally clamped discs. The discs are excited into resonant vibrations with zero, one, or two nodal diameters. It has been shown that Southwell's theory can be applied to polythene discs which are approximately 1/16 inch thick and which have diameters in the range 4 to 2½ inches. Results have also been obtained for a 4-inch diameter disc where the centrally clamped area is gradually increased from 3/8 to 2¾ inches diameter.

The technique is a new means of measuring dynamic Young's modulus and dynamic loss in flexure that is simple and rapid in operation. A report giving full details of the apparatus and results obtained for four grades of polythene is being prepared.

Compression Moulding of Polyethylene

UNCLASSIFIED

The technique of compression moulding of polyethylene into sheets was investigated with a view to producing better test-pieces than those obtained by injection moulding. The range of polyethylenes used, covered two levels of density (0.950 to 0.955 and 0.957 to 0.965) and three broad levels of melt index (1.0, 4.2, and 7.5). The method adopted was to melt the polyethylene on aluminium sheet and apply pressure gradually to the mould. Up to the final pressure of 1¼ tons per square inch and mould temperature of 310°F (154°C), the press was lowered and raised several times and then the mould was allowed to cool under pressure.

/Different

Different sheets moulded from the same batch of polyethylene differ in density according to the actual conditions of moulding, but the density was constant in any one sheet. The density variation across any one sheet as measured by means of a density column was less than 0.002 g/ml.

7.1.3 Rubbers

Permeability of Elastomers to Organic Liquids

UNCLASSIFIED

A "weight-loss" apparatus for measuring permeability of elastomers to organic liquids was developed and it was found that on using the standard test fluid mixture of 30 parts by volume of toluene and 70 parts by volume of iso-octane with a nitrile rubber diaphragm some variability was experienced. This has been found to be due to the preferential diffusion of toluene. The apparatus has been modified and, by replacing with a fresh mixture of standard test fluid daily, more consistent results have been obtained.

The Effect of Gasoline Vapour on Nitrile and Neoprene Vulcanizates

UNCLASSIFIED

Both rubbers have been shown to swell in vapour directly above the solvent and on penetration of the solvent vapour through a rubber diaphragm. A report is being prepared.

Fluorinated Elastomers in Oil

UNCLASSIFIED

With the introduction of disc brakes, the hydraulic fluid temperatures have risen considerably and fluorinated rubbers have been recommended to replace nitrile rubbers, but the short-comings of the fluorinated rubber suggest that corrosion and shrinkage may take place. Rings of vulcanized fluorinated rubber (2.6 cm. diameter) were stretched on to a polished mild steel rod (3.1 cm. diameter) and the jig subjected to 10 cycles comprising heating to 230°C, maintaining that temperature for one hour, and cooling to room temperature. After the test the metal rods did not show any corrosion; the rubber rings had a high permanent set and had increased in volume by approximately 4 per cent. One of the jigs had a metal sleeve fitted over the rubber ring and after 5 cycles of heating and cooling the outer sleeve slipped off easily indicating that the rubber ring was no longer sealing.

Sealing Rings for Tank Turrets

CONFIDENTIAL

Sealing rings were reported to be failing at the valve stem. Examination of the rings showed that the rubber was in good condition and not swollen by oil or grease. It was thought that the failure was mechanical and caused by the rings being oversize or the valves not being properly seated.

Estimation of Service Life of Nitrile and Neoprene Rubbers

UNCLASSIFIED

A survey of recent literature (from 1955) is being made to ascertain if a reasonably reliable estimate can be made of the Service life of nitrile and neoprene rubbers under a variety of environmental conditions.

/Natural

Natural Rubber Vulcanizates for Electrical Insulating Purposes

UNCLASSIFIED

The Engineering Standards Co-ordinating Rubber Committee is preparing a specification for a series of natural rubbers for electrical purposes. Five grades have been prepared by A.M.L., D.C.I. and E.R.D.E. Vulcanized sheets from each laboratory are being tested and results will be compared.

7.1.4 General Polymer Investigations

Model Polymers

UNCLASSIFIED

(a) End Groups

As might be expected the hydroxyl end-groups in the model polyethers, previously described, exert a considerable influence on physical properties. Suitable end-groups having the least influence would be the alkyl groups corresponding to the repeat units between the ether linkages. The replacement of hydroxyl end-groups by alkoxy groups by means of a reaction between the disodium salt of the model polymer and the corresponding alkyl halide does not give a very good yield, mainly because of the difficulty of forming the disodium salt and because of its instability; better results have been obtained by first converting the hydroxyl groups to acetyl groups and then reacting the product with excess alkyl halide in the presence of powdered sodium hydroxide.

(b) Synthesis

The stepwise synthesis of model polyethers is slow and tedious and a more rapid method is desirable. The method described by Hibbert (1936) whereby ethylene glycol is self-condensed in the presence of a trace of iodine to give a mixture of model polyethylene glycols capable of separation by fractional distillation has been investigated in regard to its applicability to higher glycols. Propane diol did not appear to react, butane diol cyclised to give tetrahydrofuran, pentane diol cyclised to give tetrahydropyran, hexane diol gave a small amount of the cyclic hexamethylene oxide and a high yield of model polymers which subsequently condensed further to give high polymers. The method is therefore promising for hexane diol and higher diols. A further development is the discovery that, when a mixture of hexane diol and hexyl alcohol was used, a slow reaction occurred which yielded model hexamethylene oxide polymers with the desirable hexyl end-groups. The potentialities of this method are being further investigated.

High Molecular Weight Polyethers

UNCLASSIFIED

The preparation of polytetramethylene oxide has been fully investigated using phosphorus pentafluoride as catalyst and this aspect of the work has been concluded. The results are to be published later. Apparatus for fractionating the polymers is now in operation.

/New

New Polymers

UNCLASSIFIED

Work on the attempt to prepare a polymer with semiconducting properties through polymerisation of nitrile acetylene has been resumed. An improved apparatus for separating propiolamide from yellow oil (a stage in the preparation of nitrile acetylene) has been satisfactory. Investigation of the solid left when propiolamide is removed from the yellow oil has been investigated, it appears to have the empirical formula $C_6H_4N_2O_3$ or C_3H_2NO and to have no double or triple bonds readily reduced by catalytic hydrogenation. It is virtually insoluble in all ordinary solvents except water.

Synthesis of Heat Resistant Polymers, Yarsley Research Laboratories Ltd.

UNCLASSIFIED

Synthesis of Polysulphonic Anhydrides

Various methods for the preparation of polysulphonic anhydrides from aromatic disulphonic acids have been studied in detail. The best method appears to be by polymerisation of the mixed acetic aromatic disulphonic anhydride (with elimination of acetic anhydride). The products are not of high molecular weight (degree of polymerisation, (d.p.) 10 - 15 units) and at moderate temperatures undergo a rearrangement involving migration of a sulphonic acid group with concomitant formation of a sulphone group, further (Friedel Crafts) condensation then occurs to give a three-dimensional network. The mechanism of this degradation process was elucidated by a study of model compounds. Attempted minimisation of the unwanted reactions by methylation of the aromatic nucleus led to a reduction of d.p. A brief investigation of the use of polysulphonic anhydrides as laminating agents, in an attempt to utilise the cross-linking reaction, was carried out using asbestos and glass fillers. It was concluded that the thermal and hydrolytic properties of these polymers were inadequate for high temperature use.

Synthesis of Polyamides Based on Phenazine

Preparation of polymers from dibasic acids (e.g. adipic and terephthalic) and dihydrophenazine by various methods was attempted but found to yield products of low d.p. Additionally, study of both polymers and model compounds showed that these materials eliminated phenazine on heating. In an attempt to reduce this facile elimination the use of fluorinated diacids and of 1,2,3,4-tetrahydroquinoxaline were studied. No useful products were obtained.

No further work along the lines studied is at present envisaged and termination of the contract is being considered.

Studies of Polymers under High Speed Stressing

UNCLASSIFIED

The tensile strain behaviour of a number of thermoplastics under straining velocities of 140 inches/sec. using the modified 120 ft.lb. Izod impact machine has been determined from high-speed photographs (Fastex camera at 12,000 frames/sec.). Dumb-bell specimens of CAB, Penton, polycarbonate, PVC.s and Nylons were used having as gauge marks

/aluminium

aluminium deposited on the surface in five parallel and equidistant lines. The extensions in each of the four sections so defined, and the overall extensions, have been plotted against frame number (which is directly proportional to time). Generally, extension is shown to be uniform over the four sections up to yield or brittle fracture, whichever is applicable. Beyond yield, extension is confined to the sections in which cold-drawing (i.e. "necking") occurs. The results of earlier work were given at a Symposium the proceedings of which are now published as Society of Chemical Industry Monograph No. 17, 1963 with the title of "Techniques of Polymer Science".

The effects of straining rate and low temperature on the tensile properties of Penton degraded by irradiation have been determined and the results used to elucidate the ductile-brittle transition. This work has been prepared for open publication. A detailed examination of the tensile and flexural properties of polycarbonate degraded by irradiation has been made and their relationship to molecular weight is being investigated. The above work on Penton and polycarbonate is part of a current programme on irradiation degradation studies, other aspects of which are reported on pp. 42 and 43.

Nine polythenes of differing molecular weights and densities have been successfully compression moulded and conventional tensile tests carried out. Fracture energy has been measured at a straining velocity of 300 inches/sec. using the rotating arm high speed tensile machine. Further measurements are being made at a velocity of 150 inches/sec. The fracture energy decreases with increasing Melt Index (i.e. decreasing molecular weight) and brittle fractures occur for the highest values of Melt Index.

The method of reduced variables (based on the Williams-Landel-Ferry transformations) has been applied with reasonable success to data obtained at different temperatures for the following thermoplastics. Curves at various temperatures for PMMA (tensile strength v. fracture time) and CAB and PVC/PVA copolymer (fracture energy v. strain rate) appear to superimpose satisfactorily.

The new moulding tool specifically for tensile impact dumb-bell specimens has been used to obtain specimens of polycarbonate. This thermoplastic is somewhat difficult to injection-mould and systematic changes in moulding conditions are being investigated to produce dumb-bells with a minimum of internal strain.

The Endurance of Polymers under Prolonged Load

UNCLASSIFIED

The apparatus previously described has been used to determine the life of 250-denier nylon monofil under 650-g. load in atmospheres of dry nitrogen and oxygen at 25°C. The mean lives of 60 monofils in each atmosphere are 17.1 hours in air and 15.3 in nitrogen but the wide range of results (1 - 60 hours) and the high values of standard deviation (approximately 10 in each case) dictate that considerably more experiments will be necessary to obtain statistically significant figures. An apparatus has therefore been constructed which permits 30 experiments to be conducted simultaneously. This apparatus will permit exclusion of light and the use of evacuated tubes so that the influence of stress alone may be determined.

/The

The Effect of Temperature, Rate of Deformation, and other Variables on the Physical Properties of Fibre-forming Polymers UNCLASSIFIED

This is a new E.M.R. contract with the Cotton, Silk and Man-made Fibres Research Association, and is intended to continue and widen the scope of the former contract on the behaviour of yarns and fibres at very high strain rates. A study is being made of the detailed effect of strain rate on the stress/strain curve at 20°C and 65 per cent r.h. on one yarn from each of the polymer classes: nylon 66, cellulose, polyester and acrylic. The behaviour of polypropylene has already been studied. The most recent work has been concerned with nylon 66, using a 34-filament yarn of 7.7 tex, on which stress/strain curves have been obtained at strain rates from 1.8×10^{-4} to 3×10^2 sec⁻¹. An analysis of the results, in which the stress required to produce a given strain was plotted against strain rate, showed that the curves could be divided into three sections:

- (i) At strain rates up to 4×10^{-1} sec⁻¹ the stress increased linearly with log. rate.
- (ii) At strain rates from 4×10^{-1} to 10^1 sec⁻¹ there was a "plateau" region in which the stress was insensitive to changes in rate.
- (iii) At strain rates above 10^1 sec⁻¹ the stress increased very rapidly with increasing rate.

The observed behaviour was very similar to that already found for polypropylene and it was thought unusual that the rate of change of stress should change in the same manner for two quite different materials. Thermal effects were thought to be the explanation, since materials of similar dimensions were used and thus the rates of heat loss would be similar.

The Permeability of Polymer Films to Water Vapour: UNCLASSIFIED
E.M.R. at Imperial College, London

The aim of this investigation is to study the effect of one of the many controlling factors, that of the chemical structure of the polymer chain, on the moisture permeation and sorption behaviour of polymeric films. Most of the work to date has dealt with the diffusion of water vapour in polydimethylsiloxane and polyphenylmethylsiloxane rubbers, an important feature of which is that there is a marked decrease in the diffusion coefficient as the water vapour in the polymer is increased. The results are explained in a semi-quantitative manner by assuming polymerisation of the water molecules in the polymer. In future work, a high-sensitivity balance will be used to study the diffusion of water in other polymers.

Degradation of Polymers UNCLASSIFIED

A vacuum-line assembly has been constructed for a study of the thermal degradation of model compounds of polymers containing carbonyl and ether groups (e.g. polycarbonates and polyethers) from which it is hoped to elucidate the strengths of the weakest bonds in the polymer

/chains

chains. It is intended to correlate these bond strengths with the activation energies obtained from work in progress on the thermal degradation of the polymers in bulk and in solution.

Some earlier results of these experiments on the degradation of polycarbonates have been published (J. Polymer Science, 1963, A1, 1671). More recently, advantage has been taken of the ready accessibility, through irradiation, of polycarbonate specimens of a wide range of molecular weights, but otherwise identical, in a detailed examination of the changes in flexural and tensile properties accompanying changes in molecular weight (see also pp. 41 and 42). As in the case of poly-3,3-bis(chloromethyl)oxacyclobutane (Penton), it has been found that the pattern of behaviour of each property (strength, deflection, and modulus) in flexure is closely similar to that of the corresponding property in tension although the flexural results are characterised by a greater consistency and reliability.

The study of the radiation-induced degradation of Penton has now been completed and prepared for publication. The chemical changes occurring have been attributed to chain scission accompanied by the formation of terminal unsaturation and allylic chlorine groups. The nature of the tensile strength/radiation dose curves obtained for the degraded material at various rates of straining were examined in detail and related to the shape of hypothetical brittle-strength curves. The effects of radiation, speed of stressing, and temperature on the brittle strength of the polymer have also been determined.

Autoxidation of Polymers

RESTRICTED

The model substances for polyolefin and polyamide autoxidation were the same as previously described except that 2,2',4,4',6,8,8'-heptamethylnonane was replaced by 2,6,10,14-tetramethylpentadecane. A recording apparatus suitable for the examination of antioxidant efficiency at high temperatures was built (Martin apparatus) and some tests were carried out at 100°C. It was found that the protection factor of the newly developed 3',4',5'-trihydroxy-4"-t-butylpolyporic acid (BTHP) for hexadec-1-ene was at least twenty times larger than that of Ionol, thus confirming the expectation based on the previously reported experiments with metal catalysts at 50°C. 3',4',5'-trihydroxy-3",5"-di-t-butylpolyporic acid did not prove superior to BTHP in antioxidant efficiency or solubility in non-polar media. The development and testing of new antioxidants is continuing.

The previously reported anomalies concerning autoxidation in the solid state were confirmed in the γ -ray-induced autoxidation of thin films of docos-1-ene (thickness varying between 4 and 150 μ) on silica tubing or gold foil. The overall rate of radiation-induced autoxidation of these films at 25°C was found to be about thirty times larger than that of homologous liquid alk-1-enes, e.g. hexadec-1-ene, at the same temperature. Similar observations concerning the relatively fast rate of solid state autoxidation of olefins were also made in a metal-catalysed system.

/It

It was found that bis(N-butylsalicylaldimino)-cobalt(II) exhibited an irregular concentration effect in the catalysis of alk-1-ene autoxidation at 50°C; there was an optimum efficiency at a catalyst concentration of M/2000. At this concentration and temperature the cobalt compound was also shown to be a powerful autoxidation catalyst for the saturated 2,6,10,14-tetramethylpentadecane which because of its tertiary C...H bonds is being used as a model substance for polypropylene. The kinetic details are being examined.

The susceptibility of polyamides to photo-induced autoxidation made it desirable to find a suitable system for a basic study of model amides. The only relevant investigation reported in the literature is confined to light of wavelength as low as 254 mμ and is therefore of little practical significance. On the assumption that trace metals play an important role even in the photo-induced autoxidation, experiments were carried out with deliberately added metal compounds, particularly metal acetylacetonates, the photochemistry of which has hardly been explored. Light of 365 mμ wavelength was used and it was found that under these conditions ferric and cobaltic acetylacetonates were photocatalysts for the autoxidation of N-methyl acetamide (as well as hydrocarbons). The details of the mechanism of this interesting photocatalysis are being studied and experiments are also proceeding with a view to developing for this photo-sensitized reaction suitable inhibitors which could be of wider practical significance in the field of light stabilization.

A new antioxidant, 3-(3,5-di-t-butylphenyl)-2,5-dihydroxy-6-(3,4,5-trihydroxyphenyl)benzoquinone, has been synthesized. Manganese phthalocyanine was prepared, and purified by sublimation in vacuo at 650°C.

Non-Metallic Projectile Driving Bands

CONFIDENTIAL

The hoop strength (5250 p.s.i.) of the polyacrylonitrile fibre epoxypolysulphide resin bands sent to R.A.R.D.E. for a firing trial proved insufficient to ensure retention of the band: work on this system has been discontinued. Bands made from self-bonded polyacrylonitrile fibre, using water and dimethylformamide as swelling agents, have shown hoop strengths less than that quoted above. Attempts are now being made to limit the swelling action to the surface of fibres, to obtain adequate bonding without the loss of fibre strength which accompanies complete swelling. The introduction of voids into these structures to improve engraving in the barrel is being attempted by incorporating calcium alginate fibres during fabrication, followed by their removal by boiling in dilute aqueous alkali. It is believed that the presence of voids will also reduce the high radial pressures exerted by bands on the gun barrel during firing.

Compatibility of Rubbers with Plastic Explosives

UNCLASSIFIED

Nitrile and neoprene rubber vulcanizates are being tested against the plastic explosives PE4 and PE6A, an experimental plastic sheet explosive and the high explosive tetryl.

/After

After 3 months trial the tensile strength of the rubber sheet in contact with the three plastic explosives was within 10 per cent of the original values. With tetryl, however, the tensile strength of the neoprene decreased by about 10 per cent and that of the nitrile rubber increased by about 20 per cent. The elongation at break of both rubbers was reduced in all instances. The reduction was greater when in contact with tetryl. The elongation at break of the neoprene was reduced from 430 to 300 per cent and that of nitrile rubber from 430 to 50 per cent. The trial is continuing.

Environment Trials of Plastics

UNCLASSIFIED

The following plastics have been subjected to environmental trials, Lexan, Makrolan, Delrin, Penton, Diakon LO, Diakon MO, Propathene HWM-05, Propathene LWP-09, Propathene GWM-02, Cyclocac T1000, Kralastic 553/601, Tyril 767, Bextrene BC/15/9158 and Bextrene BC15-1/9158. Each material was tested at intervals up to 12 months at 70°, 90° and 100°C in a dry atmosphere, 70° and 90°C at 100 per cent relative humidity and at 90°C immersed in water. The trials are now complete and a report is being prepared.

Compatibility of Plastics with Explosives

UNCLASSIFIED

Test pieces of the following materials have been prepared, Rigid PVC, Delrin, Makrolan, Lexan, Propathene LWFO9, Propathene GWM-02, Propathene HWN-05, and tested at 60°C in contact with TNT, RDX/TNT, propellant NQ and propellant NH. Three modifications of polystyrene and two ABS copolymers have been tested at 60°C in contact with TNT and RDX/TNT only. The tests are now complete and a report is being prepared.

Evaluation of New Materials

UNCLASSIFIED

New materials in the plastics and rubber field such as Hostaform C, a polyacetal/dioxane copolymer, and Neoprene ILA, a copolymer of chloroprene and acrylonitrile, have been obtained for evaluation.

Neoprene ILA was evaluated using a recommended mix. Increasing the accelerator content from 1.5 parts per hundred of rubber to 4 parts it was found that there was a maximum tensile strength at 3 parts and a slight reduction of elongation at break in all instances. The addition of sulphur without accelerators gave "peaky" cures and the highest tensile strength was obtained with 0.25 part. The addition of 0.25 part of sulphur to the base mix containing 1.5 parts of accelerator gave a vulcanizate with the best physical properties.

The work on Hostaform C has not yet started.

Decomposition of Polyacetal Moulded Components

UNCLASSIFIED

Previous tests have shown considerable decomposition of polyacetal moulded components as indicated by a loss in weight of 37.5 per cent after 30 weeks at 70°C and 100 per cent relative humidity. The temperature of the test was reduced to 60°C and, to date, after 25 weeks at 100 per cent relative humidity there has been a slight increase in

/weight

weight of 0.5 per cent, and at 70 per cent relative humidity an increase in weight of 0.1 per cent. No visible signs of decomposition have been observed.

Fibre-Glass Torpedo Warheads

CONFIDENTIAL/DISCREET

A Canadian torpedo warhead made from an epoxide/glass laminate shell, with polyester/glass laminate bulkhead and end plates, and a polyurethane lining system, has been subjected to a climatic trial. The warhead, filled with high explosive, was stored 6 months under I.S.A.T.(A) conditions and 12 months at 140°F (60°C).

After 6 months climatic storage the tensile strength of the liners and the epoxy laminate has slightly decreased, and that of the polyester laminate has slightly increased. After 12 months the decrease in tensile strength was slightly greater for the liner and little further change in the epoxide and polyester laminates occurred. The changes in elongation at break of all plastics were insignificant.

Stress Cracking of Polymers

UNCLASSIFIED

As assessment of cracking and crazing of various polymers under stress and in contact with various solvents has been made. It would appear from the present results that the absorption of the solvent by the polymer is more important than the solubility of the polymer in the solvent.

Fractionation of Polymers

UNCLASSIFIED

Phase diagrams have been established for the system acetone/cyclohexanone/polyester using (a) a linear polyester (b) a highly cross-linked polyester. With the linear polyester, separation by molecular weight is not difficult but with the cross-linked polyester, the solubility depends on the degree of crosslinking as well as the molecular weight, the highly cross-linked material being less soluble. This is likely to be a disadvantage in exploitation of the technique.

7.2 ADHESIVES AND SEALANTS

Torsional Shear of Annular Joints

UNCLASSIFIED

The statistical analysis of the results obtained with adhesive M.S. 9160 (a cold-cure silastomer) in metal-to-metal annular joints has continued. More detailed examination has shown that, contrary to the statement in Technical Report TR.2/62, the failing stress is independent of the annular width of the joint, other things being equal. The tests were always carried out at a substantially constant rate of movement of one ring relative to the other, so that increasing the glue-line thickness has the effect of decreasing the shear strain rate. The decrease in failing stress with increasing glue-line thickness may be associated with this. Further experiments are planned to investigate the effect of shear strain rate on failing stress over a wide range of rates.

/Test-pieces

SECRET/DISCREET

Test-pieces in the form of cylinders to be butt-jointed and broken in torsion have now been delivered. The results obtained with these will be compared with corresponding results with annular joints and with butt-jointed cylinders broken in simple shear.

Adhesive Strength of Lap Joints: E.M.R. with Royal College of Science and Technology, Glasgow UNCLASSIFIED

The improvements predicted from theoretical analysis in joint strength obtained by using correctly bent lap joint members are now being tested practically. The college is however still having difficulty in getting reproducible joint strength results and it is proposed to collaborate in tests of practical joints at E.R.D.E.

Stress Distribution in Adhesive Joints UNCLASSIFIED

It has been shown experimentally that when a lap joint between metal and a low modulus rubber is stressed the stress concentration in the adhesive at the free end of rubber at the joint is virtually zero. In many cases of failure of a lap joint under stress, breakdown occurs by peeling due to stress concentrations at the free ends of the overlap. The possibility of reducing such failures by investigating standard and double lap joints whose elastic moduli are in the ratio of 10:1 is being investigated.

Adhesion of Rubber Proofing to Cloth UNCLASSIFIED

The method of measuring the strength of the bond between rubber and cloth, by a tensile force normal to the interface has been investigated and used for some time. It has now been specified for testing Dracone cloth and proofed fabric for military clothing, and has been used successfully to control manufacture for Government contracts.

The further investigation of this method to measure the influence of chemical bonding agents, design of fabric, curing conditions etc. on bond strength is dependent upon the availability of a suitable student at the National College of Rubber Technology with whom an E.M.R. contract has been placed.

Adhesives for Cured Nitrile Rubber UNCLASSIFIED

The comparison between a proprietary nitrile-based adhesive, a proprietary polyurethane-based adhesive and a 50/50 Epikote 828/Versamid 140 formulation has been completed by examination of the resistance of the bond between nitrile rubber surfaces to exposure to water for one month at 40°C.

Under these conditions, the nitrile-based polymer loses 20 per cent of its original bond strength, the polyurethane loses 75 per cent, but the Epikote/Versamid remains unchanged. This last adhesive is, however, too rigid for use with rubber-proofed fabrics. The possibility of improving its flexibility is therefore being examined.

/Sealing

Sealing Threaded Joints

UNCLASSIFIED

- (i) A report on thread-sealing investigations with polytetrafluoroethylene tape and cord has been completed and published (E.R.D.E. Technical Memorandum No. 16/M/62). Publication also in the open literature is probable.
- (ii) A report on studies of commercial lutings has been drafted, and one on commercial cements is almost complete.
- (iii) It was stated in D.M.X.R.D. Report No. SEAL/59/1, which described experiments with surface-catalysed compounds, that one of higher viscosity than those then examined (maximum viscosity 1 poise) should be an outstanding sealant. Consequently, the manufacturers (American Sealants Co.) have now produced a material of viscosity 20 poises, which is approaching the desired minimum of 50 poises. This new material will be examined as a thread sealant as soon as possible. The sealing properties of a new range of surface-catalysed compositions produced by a British firm will also be examined.

7.3 CERAMICS AND REFRACTORIES

UNCLASSIFIED

Refractory Fibres and Films for Reinforcement

Fibres - Production of Si_3N_4 Whiskers

Substantial advances have been made in the operation of the semi-scale furnace and both the quantity and quality of the whiskers has been much improved. Above all, the operation is more consistent. This has been achieved by a number of changes, notably the addition of stoichiometric quantities of SiO_2 to the silicon source to provide SiO carried in argon as the transfer medium for silicon. The provision of mullite ($\text{Al}_2\text{O}_3.\text{SiO}_2$) substrates is also very beneficial. We think that this process could now be operated on a commercial scale.

Films

A theoretical study has been made of the conditions for the growth of carbide films and a furnace for making SiC film materials is under construction.

Preparation of Experimental Two-Phase Materials

Whiskers/Metal Systems

Materials made from Si_3N_4 whiskers bonded with both nickel and silver have been prepared. Silver is useful as a model material because it creeps at room temperature and this enables the effect of reinforcing fibres on the creep of a refractory metal at high temperatures to be imitated at room temperature.

/So

So far these materials have been made by adding finely powdered metals to a felted mat of whiskers and sintering the mixture under pressure. However, we are now trying to coat the whiskers with a continuous film of metal instead of adding a powder, for two reasons:

- (i) To get better packing and control of the fibre orientation it is necessary to card the fibres into parallel bands and when this is done the powder method cannot be used.
- (ii) In the case of such metals as aluminium, which would benefit by being reinforced with whiskers, the powder method cannot be used because of the oxidation of the metal particles.

Simultaneously with this work we are examining methods of preparing parallel bands of whiskers which will probably be necessary if efficient materials are to be achieved.

Plate and Film Systems

We are making a few models of plate reinforced systems, notably in high tensile steel foil bonded with aluminium.

Mechanical Behaviour of Two-Phase Systems

We have now computed the solution of the problem of a crack meeting an interface in a two-phase system. In order to stop the crack the adhesion of the interface must be less than one-fifth of the cohesion. A model illustrating this principle has been made and exhibited at a Royal Society Conversazione. Further investigations are in progress.

7.4 ELECTRONIC MATERIALS

UNCLASSIFIED

Study of Epitaxial Growth of Crystalline Films for Semi-Conductors and other Devices

Gallium Arsenide

An E.R.D.E. Technical Memorandum, No. 15/M/63, on the theoretical analysis of the chemical transport process for the deposition of gallium arsenide is being prepared.

Zinc Sulphide

A similar study of the growth of zinc sulphide crystals has been computed and will be reported.

Experimental work to confirm these analyses is in progress.

/8

8.1 UNIT OPERATIONS

Crystallisation

UNCLASSIFIED

The study of abrasion processes for producing spheroidal crystals has been continued. Whilst a number of methods can give a desired product, there is a wide variation in their effectiveness. For example, under certain conditions stirring has a slow rounding action, as does the passage of a slurry past an inclined plate. The circulation of liquid through a tube normally results in a slow rounding action, but at suitable slurry densities with narrow tubes rapid spheroidisation occurs, with minimum fracture of the crystals. The most perfect rounding action, though not the most rapid, has been achieved with an undulating tube using crystals in the 50 - 200 micron range. A more recent form of apparatus has produced 1 lb. of spheroidised crystals in 10 minutes.

Research on the performance of an Oslo-type crystalliser under E.M.R. contract at Birmingham University has continued on a magnesium sulphate/water system. Liquor temperature and concentration measurements were made at different points in the bed, and growth rates and mass transfer correlations calculated. It was found that secondary circulatory currents interfered with good classifying action, and that most crystal growth, by relief of supersaturation, took place near the bottom of (inlet to) the bed.

Non-Newtonian Liquids

UNCLASSIFIED

In an E.M.R. at Swansea University, an apparatus, consisting of a vertically mounted, cylindrical, mixing vessel with anchor agitator, has been set up to study the mixing of non-Newtonian liquids. The agitator and variable-speed motor are suspended so that the torque and hence power input can be measured, and a capacitance probe has been developed to measure the degree of mixing with time at selected points. In a new E.M.R. at King's College, Newcastle it is planned to study heat transfer to non-Newtonian fluids flowing in an electrically heated pipe. This will involve recirculation of the liquid with external cooling, and measurement of temperature and velocity profiles across the pipe section. Both these investigations will use pseudoplastic liquids of the carboxymethyl cellulose type at first, after initial calibration with Newtonian liquids, though the use of viscoelastic liquids is a possible longer-term aim.

Mass Transfer on Spiral Spring Packing

RESTRICTED

The spiral spring drying column for nitric esters is applicable to any liquid of low vapour pressure and may be used in any liquid/gas mass transfer operation where low pressure drop is desired. Mass transfer is being measured with liquids of different physical properties and at different flow regimes on the wire packing. Photographic studies show that there are three stable flow states with a smooth transition from one to the other. Initially, at low flows, there is

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a near-film flow down the spiral spring wire which, at higher flows, develops into droplet transport down the wire at constant velocity if the pitch of the spiral is uniform. At a high rate of liquid flow the droplets change to a necked form in which they have a greater velocity down the wire and tend to lose their hold and escape from it. This is near the "flooding point" of the column where the characteristics change radically and the column acts more as a spray tower.

In addition to the above studies, mass transfer coefficients for water vapour diffusion into and out of low-vapour-pressure liquids have been determined using a static film on a recording balance specially adapted for the work, so that temperature and humidity can be controlled. Values have been obtained for TEGN, dimethyl phthalate and mixtures of these with polyester at 20°C and 60°C. The mass transfer coefficient for the stagnant film is naturally low and it falls into the range 0.1 - 0.3 lb/hr.ft².atm. for TEGN/polyester mixtures. The values are almost unchanged by the temperature in the range 20° to 60° C and, although possessing similar viscosity and density, dimethyl phthalate shows a considerably lower coefficient than TEGN.

8.2 EQUIPMENT STUDIES

Propellant Mixers

UNCLASSIFIED

The instrument which has been developed and constructed to measure the clearance between agitator blade and the wall of an empty mixer was described in the previous Technical Report; and it was explained that this, used in conjunction with an instrument which measures the agitator shaft deflection outside the mixer when the mixer is in operation, will indicate the blade/wall clearance in the operating mixer, which is important for safe operation.

The shaft deflection monitor has been developed incorporating a sensing unit made by Sigma Instrument Company. The sensing transducer unit is mounted outside the gland of a mixer shaft and two sensing elements touch and follow the shaft surface in two directions at right angles on an accurately prepared datum surface. A follower moves a ferrite core differentially in two inductors which form the limbs of a bridge circuit, the out-of-balance being proportional to the shaft deflection in that direction. This signal can be displayed on an indicator, recorded on a ultraviolet-sensitized chart giving an immediate trace, or used to operate warning or shut-down systems. The linear range of the transducers is 0.010 inch with resolution better than 0.0001 inch.

These equipments have been tested on experimental rigs, and are now being applied to trials on a 60-gallon, twin-bladed, Baker Perkins, vertical mixer.

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Flow of Powders

UNCLASSIFIED

Continuing the investigation on dense-phase fluidized transport and bulk storage of fine powders, (over 100-micron to sub-micron particles), a pulsed flow technique has been developed in which the fluid is admitted to the bed in pulses of controlled frequency and duration. In the 12.0-inch diameter glass storage vessel, this gave increased overall bed activity, with no inactive regions and no tendency to channel or spout. The best pulsing technique is being investigated and different powders used (e.g. cement, talc, and titanium dioxide) to evaluate the effect of density and other powder characteristics. Commercially available porous plates are also being evaluated as air distributors. An air/water model has been used in some of this work to assist in studying air distribution.

Hydraulic Transport of Hazardous Materials

UNCLASSIFIED

Tests have been made on transporting a cylindrical capsule or vehicle in controlled water flow in a pipe, primarily as a means of transporting sensitive or dangerous materials. Pipes used have been plastic hose up to 1-inch bore arranged in a circuit of varying path and heights, and the vehicles have varied from heavy glass-tube capsules to light aluminium cylinders, with cross-sectional area from 0.6 to 0.9 of that of the pipe bore and length to diameter ratio of about 6 to 1. Transport appears easy and controllable. The advantages visualized for such a system are that it is applicable to any distance or levels (within a wide range), and any path or contour so that it can be quickly and cheaply laid down. The speed of transport and avoidance of shock are easily controllable and the passage of the vehicle can be monitored; delivery of the vehicle into and receipt from the pipe line can easily be arranged. Any detonation of a capsule would be cushioned by the transporting fluid and flexible nature of the pipe. A recent paper (G.W. Hodgson and M.E. Charles, Canad. J. Chem. Eng., 1963, 41, 43 - 51) demonstrates mathematically the theory of encapsulation transport and our experimental evidence supports this theory.

Mass Flowmeter

UNCLASSIFIED

The principle of the gyroscopic pipe flowmeter has been studied to determine if the sensitivity of the system could be extended to better than ± 0.25 per cent of full scale deflection. The study confirmed mathematically that the output torque is proportional to the mass flow rate. It also confirmed the gyro theory and showed that the forces involved in producing the output torque in the loop are also present if the material is flowing through a straight pipe ('X' axis), if the pipe is driven with a rotary sinusoidal movement about an axis at right angles to the pipe midway along its length ('Y' axis). The resulting output torque is measured about the 'Z' axis at right angles to the sinusoidal input. Considering the engineering work to produce a straight pipe flow meter, against that required to construct a complete loop, it was decided to build a straight pipe prototype meter for evaluation. Trials have been conducted working at a drive frequency of 10 cycles/sec. and peak angular movement of 3° with a flow rate of approximately 60 lb/min. An average output force of 6 ounces was obtained. This confirmed the principle of operation, but a new rig

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is being constructed to eliminate pipe connection loadings and give a more sensitive instrument.

Inspection and Extraction of "Silvered Vessels"

UNCLASSIFIED

In the climatic testing of propellants, samples in silvered calorimeter vessels are kept under surveillance at 80°C. Galvanometer readings which compare the temperature with a reference standard, by thermocouple readings, are taken 3-hourly day and night to detect samples which are becoming unstable.

An automatic inspection equipment has been developed to inspect 20 samples, every 10 minutes. A 20-point scanner selects each thermocouple in turn and compares it with the reference thermocouple. A differential temperature rise of 2 degC deflects the galvanometer spot across a photo-conductive cell, which operates a relay and causes extraction of the sample from the climatic test cell. The equipment has been tested successfully with a number of propellants.

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9.1 CHROMATOGRAPHY

Gas Chromatography

UNCLASSIFIED

The use of amines to break down colloidal propellants, and so obtain solutions suitable for analysis by gas chromatography, has been further studied. Satisfactory methods for the estimation of methyl and ethyl centralites, and dimethyl, diethyl and dibutyl phthalates have already been reported. Diphenylamine and 4-nitro-N-methylaniline (4-NMA) have been estimated satisfactorily after solution of the propellant in a 1:1 mixture of ethylene diamine and ethanol. The N-nitroso derivatives of both compounds are converted quantitatively to the parent amines by this treatment, and cannot be distinguished. Thus, in the case of 4-NMA whose nitroso derivative is not regarded as an active stabiliser the method is not considered suitable for the estimation of residual stabiliser in aged propellants. For diphenylamine, it gives the same answer as the methods at present employed, which also estimate diphenylnitrosamine plus the amine.

Attempts to estimate triacetin and dinitrotoluene by similar methods were unsuccessful, both compounds undergoing partial reaction with the amines. However, a suitable method for triacetin by chromatography of a solvent extract of the propellant has already been reported, and dinitrotoluene can be determined similarly. These gas chromatographic procedures have been applied successfully to all types of colloidal propellants, and are particularly useful for determinations of small proportions of stabilisers, for the analysis of compositions containing two or more constituents of a similar chemical nature, for the identification of unknown ingredients, and for the analysis of compositions whose physical nature makes some of the normal analytical processes, such as solvent extraction, difficult. In favourable cases several constituents may be determined rapidly from the same chromatogram, e.g. 2,4- and 2,6-dinitrotoluene, diphenylamine and dibutylphthalate can be estimated from a solvent extract of an FNH powder.

Although it has been possible to apply gas chromatography to explosive materials of low volatility, such as nitroglycerine and trinitrotoluenes using packed columns, the quality of the chromatograms has generally been poor. The use of capillary columns, having greater resolving power, is being investigated. The usual column of this type, made of steel, and with a length of the order of 150 ft., was found to be quite unsuitable. A high column temperature was required to obtain reasonable retention times, and normally stable materials such as nitrobenzene suffered extensive decomposition, while dinitrobenzenes failed to emerge from the column. Using a shorter (30-ft.) column better results were obtained. Mono and di-nitrobenzenes and mono- and dinitrotoluenes were chromatographed successfully at 120°C with column efficiencies of 3000 theoretical plates, but the trinitro compounds, and nitric esters still decomposed before completing their passage through the column. A short (20-ft.) glass capillary column has now been obtained, which it is hoped will avoid the reaction on the metal surfaces which appears to take place with the steel columns.

/Thin

Thin Layer Chromatography

UNCLASSIFIED

The technique of micro-adsorption chromatography has been extended, especially in the field of double-base propellants.

A method has been developed for the determination of residual 4-nitromethylaniline in aged propellants containing 2-nitrodiphenylamine, resorcinol, or carbamate as well as 4-nitromethylaniline.

A method is being developed for the rapid identification of the ether-soluble ingredients of double-base propellants. To date, nitroglycerine, carbamate, dibutyl phthalate, triacetin, 2-nitrodiphenylamine, and 4-nitromethylaniline can be readily identified.

9.3 CRYSTALLOGRAPHY

UNCLASSIFIED

Tetrazene

Tetrazene Hydrobromide

The high absorption coefficient for X-rays of this substance makes it desirable to use spheres or cylinders of the crystal when recording diffracted X-ray intensities; with this provision the effects of absorption can be allowed for or in suitable cases neglected. These shapes have now been successfully produced by partial dissolution in formic acid of suitably shaped cleavage fragments of the crystal.

A complete set of Weissenberg films covering all hkl reflections has been recorded with molybdenum radiation, using crystals rotating about b or a axes. Some reflections at low angles are not accessible using molybdenum radiation with the present equipment, and these were recorded with copper radiation. The diffracted intensities measured from these films will be used for the final refinement of the structure of tetrazene hydrobromide.

Tetrazene

The conditions necessary for growth of useful crystals of the A form of tetrazene from formic acid solution have now been established. Usable crystals have been grown and a complete set of hkl-reflection X-ray intensities is now being recorded using a Weissenberg camera. When the final results of the hydrobromide structure are available, it is proposed to attempt the analysis of the A form of tetrazene; this form is chosen since it belongs to a centro-symmetrical space group.

The growth of suitable crystals of the B form of tetrazene has also been investigated. This form has been made by reaction of aminoguanidine salts with sodium nitrite in solution, using a range of concentrations. Different salts of aminoguanidine gave great differences of crystal habit. Suitable crystals have been prepared and will be used in recording the hkl-reflection X-ray intensities. At present it seems very likely that the crystals belong to a non-centrosymmetrical space-group; this circumstance generally leads to

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increased difficulty in carrying through a structure analysis, but in the present case it is expected that the structure of the B form will become evident in a very direct way from the structure of the A form, since the lattice parameters and X-ray intensities of the two forms show the existence of a very special relationship between the two structures.

Lead Trinitrophloroglucinate

Magnesium trinitrophloroglucinate is used in the preparation of the lead compound; it has been shown that a solid separating, on standing, from a solution of the magnesium salt is magnesium oxalate. Knowledge of the presence of impurities and decomposition products and their accumulation in aged solutions of reactants may provide useful clues in identifying the conditions necessary for preparation of the A and B forms of lead trinitrophloroglucinate.

9.4 RADIOCHEMISTRY

Thermal Degradation of Polymers

UNCLASSIFIED

Work has started on a study of the thermal degradation of polystyrene. Although it is generally accepted that the decomposition of polystyrene takes place by a primary bond scission followed by an unzipping process, there is uncertainty whether the primary scission is at the terminal unit of the chain, what is the average unzipping length, and whether inter- or intra- molecular chain transfer takes place during the degradation. It is hoped that light may be shed on these problems by studying polystyrenes of identical chain composition but with known end groups.

These may be synthesised by the 'living' polymer technique discovered by Szwarc wherein polystyrene molecules with anionic ends ($\sim\sim\sim \text{CH}_2-\overset{\text{PL}}{\underset{|}{\text{CH}}}^-$)

are produced which may be terminated at will with various reagents to produce the end groups desired. The technique requires that polymerisations be carried out in high vacuum, in the absence of greased stopcocks, and with exceedingly pure reagents. The method consequently presents a number of practical problems and a complete synthesis takes a number of days although the polymerisation itself is a very rapid process.

A high vacuum apparatus has been constructed and a number of 'living' polystyrene batches have been prepared at specific molecular weights ranging between 5,000 and 100,000. These have been terminated with a number of reagents to produce polystyrenes with end groups

$\sim\sim\sim \text{CH}_2 \cdot \text{CHR}$, where R is $-\text{H}$; $-\text{COOH}$; $-\text{CH}_2\text{CH}_2\text{OH}$; $-\text{CPh}_3$; $-\text{CMe}_3$; cyclohexyl; 1-naphthyl; $-\text{COPh}$; $-\text{Br}$; $-\text{I}$; allyl; and 9-(9,10-dihydroanthranyl).

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It is hoped to compare the thermal breakdown characteristics of these polymers with that of 'normal' polystyrene ($\sim\sim\sim \text{CH}_2-\underset{\text{Ph}}{\text{CH}_2}$).

Obviously if the degradation is initiated at the chain end and the unzipping length is appreciable, then significant differences in the breakdown rates should occur, at least in the initial stages. In this case, detailed study of the differences should give quantitative information of the breakdown mechanism.

At present a vacuum microbalance is being constructed to carry out these investigations.

9.5 MICRO-ANALYSIS

Determination of Boron

UNCLASSIFIED

The difficulty experienced in the determination of boron in inorganic compounds has been overcome. It was found that by careful adjustment of the amount of sodium peroxide mixed with the sample before combustion in an oxygen flask, complete combustion was achieved.

/List

SECRET/DISCREET

List of Reports Bearing the Grading "Discreet"
Issued by E.R.D.E. in the Period 1.1.63 to 30.6.63

Classification Key: S/D = SECRET/DISCREET
C/D = CONFIDENTIAL/DISCREET

Number	Classi- fication	Author	Title
23/R/62	C/D	F.W. Emery, P.L. Harold and A.J. Owen	The Thermal Decomposition of 2-Ethyldecaborane
26/R/62	C/D	J.W. Grindlay and G.J. Jeacocke; J.W. Grindlay and (Miss) A.R. Howieson	The Stability of Colloidal Propellants: Part 6: Resorcinol as a Propellant Stabiliser with Appendix: The Determination of Resorcinol
TR.2/62	S/D	-	Technical Report for the Period 1.7.1962 to 31.12.1962

/List

List of Reports and Technical Memoranda
Issued in the Period 1.1.63 to 30.6.63

Classification Key: C = CONFIDENTIAL
 R = RESTRICTED
 U = UNCLASSIFIED

Number	Classification	Author	Title
17/R/62	U	A. Davis	Solid Propellants: The Combustion of Particles of Metal Ingredients
20/R/62	U	W.A. Dukes and L. Greenwood	The Endurance of Nylon Cloth under Constant Load
21/R/62	U	G.C. Bromberger, C.P. Conduit and E.A.A. Hitch	The Significance of the Abel Heat Test
27/R/62	C	E.M.G. Cooke, F.H. Doe, B.H. Newman and J. Scrivener	Polyester Polyurethane Propellants: Summary of Work Carried out from January, 1961 to June, 1962
28/R/62	U	R.P. Ayerst and P. Coxon	An Improved Process for Ammonium Perchlorate Manufacture
7/M/62	U	D.H.L. Mansell and W.A.W. Smith	A Rapid-Response Flame Detector
15/M/62	C	C.P. Conduit	The Stability of Colloidal Propellants: Part 5: The Rates of Heat Generation and Critical Charge Sizes for a Composite Modified Cast Double-Base Propellant
16/M/62	U	W.A. Dukes and (Mrs) J.V. Long	The Sealing of Threaded Joints: Part 4: Polytetrafluoroethylene Tapes and Cord
2/R/63	U	J. Powling and W.A.W. Smith	The Surface Temperature of Ammonium Perchlorate Burning at Elevated Pressures

/Papers

UNCLASSIFIED

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Papers Published in the Open Literature
in the Period 1.1.63 to 30.6.63

Author	Title	Journal Reference	File No.
Allen, G. and Sims, D.	Intermolecular Forces and Chain Flexibilities. IV: Internal Pressures of Polyethylene Glycol in the Region of its Melting Point	Polymer, 1963, <u>4</u> , 105	WAC/ 142/017
Bellamy, L.J. and Pace, R.J.	Hydrogen Bonding in Carboxylic Acids - I. Oxalic Acids	Spectrochim. Acta, 1963, <u>19</u> , 435	WAC/ 142/031
Bellamy, L.J., Luke, R.F. and Pace, R.J.	- ditto - II. Monocarboxylic Acids	ibid., 443	
Golden, J.H. and Hazell, E.A.	Degradation of a Polycarbonate by Ionizing Radiation	J. Polymer Sci., 1963, <u>A.1</u> , 1671	WAC/ 130/047
R.W. Gooding and N.J. Parratt	Solid Titanium Nitride and other Refractory Compounds Made by Direct Gas/Metal Reaction	Powder Metallurgy, 1963, 42	WAC/ 142/040
Lewis, T.J., Richards, D.H. and Salter, D.A.	Peroxy-complexes of Inorganic Ions in Hydrogen Peroxide/Water Mixtures Part I. Decomposition by Ferric Ions	J. Chem. Soc., 1963, 2434	WAC/ 142/010
Flood, P. Lewis, T.J. and Richards, D.H.	- ditto - Part II. Decomposition by Chromate Ions	ibid., 2446	
Dedman, A.J., Lewis, T.J. and Richards, D.H.	Part III. Decomposition by Molybdate Ions	ibid., 2456	
Wright, W.H.G.	Levelling Device for the Pregl Micro-nitrometer	Chem. and Ind., 1963, 288	WAC/ 142/039

S. No. 834/63/BL/BD

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